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***Japan***

ADVANCED COMPOSITE MATERIALS  
1992 SEMINAR

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SCIENCE & TECHNOLOGY  
JAPAN

ADVANCED COMPOSITE MATERIALS  
1992 SEMINAR

936C3802 Tokyo SENTAN FUKUGO ZAIRYO SEMINA in Japanese 14-15 Jul 92 pp 1-68

[Selected papers from the Advanced Composite Materials Seminar held 14-15 Jul 92 in Tokyo, sponsored by the Japan Society of Powder and Metallurgy]

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d) Residual stress is always unwanted: Very localized residual stress does not induce destruction.

e) A grain boundary can be made only at the time of sintering: A group of dislocations can create a formable subgrain boundary.

f) Grains always need to be fine: Fine structures can easily be deformed, while larger grains have better characteristics against creep and higher toughness.

g) A homogeneous microstructure is always the best: Heterogeneous structures can produce greater toughness. But heterogeneity should not lead to an increase in destruction sources.

h) The only ways to control grain boundaries are to increase the level of purity and to make the boundary phase more resistant to heat: The grain boundary structure could be controlled by scattering fine grains in the grain boundary. A subgrain boundary made by a group of dislocations has a higher level of purity than a grain boundary made at the time of sintering.

i) Ceramic deformation cannot be curbed at temperatures higher than the temperature that is predictable from chemical bonds: Deformation at high temperatures can be curbed by controlling the transfer of dislocations.

j) The destruction of ceramics is caused by the development of a crack. The direction of crack development cannot be controlled: Stress causes cracks to develop. Therefore, the direction of crack development can be controlled even at high temperatures by introducing local stress within the material.

k) Young's modulus and the thermal expansion of ceramics can be controlled only by the introduction of vesicles and micro-cracks: Controlling them is possible with the use of amorphous and solid solutions.

l) The current sintering theory also holds true for fine grains: This is not necessarily correct. It has been reported that fine grains momentarily rotate at the time of sintering.

Based on the above points, the four kinds of nano composite structures shown in Figure 1 can be considered as structures that could sharply improve various mechanical characteristics, and add new functions to ceramics. The in-grain nano composite material can be considered using points a)~g) and i)~k), the grain boundary nano composite is relevant to point h), the nano/nano composite can be considered on the basis of points b) and f), while point l) leads to the conclusion that these

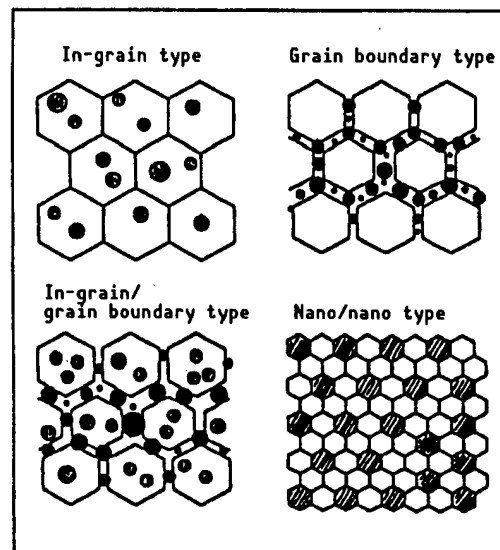


Figure 1. Type Charts of Nano Composites

three new kinds of composite materials can be manufactured by the sintering method. Further, a structure in which an in-grain nano composite and grain boundary nano composite are achieved simultaneously also can be considered. From the viewpoint of linear fracture mechanics and metallic material design theory, the in-grain nano composite, as a structural material, has the most structure. By realizing this structure, it will become possible to boost strength two to five times, for example, and to raise the temperature limit by 400~700°C. But a sharp increase in fracture toughness cannot be expected. In order to achieve super-strong and supertough ceramic materials, it ultimately will be necessary to combine micro composite materials and nano composite materials. Possible micro-nano hybrid materials include whisker-reinforced, sheet grain-reinforced, and long staple-reinforced nano composite materials (Figure 2).

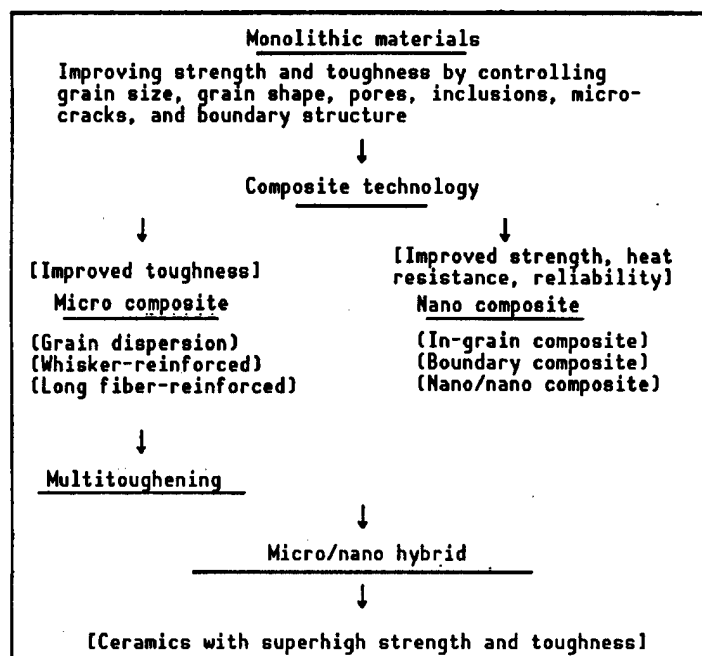


Figure 2. Development Concept for High-Performance Structural Ceramic Materials

The following describes recent progress in the sinter-manufacturing of ceramic-based nano composite structural materials, and improvements in various mechanical characteristics through the use of the nano structure and nano composites, centering on research by the author and others.

## 2. Manufacturing Nano Composite Ceramics

Chemical vapor deposition (CVD) and the precursor method are the most suitable manufacturing processes for producing a nano composite with very fine second phase dispersed inside grains, which have been considered the smallest construction unit of ceramics, or grain boundaries. However, it is difficult to manufacture large, complex-shaped structural ceramics by CVD at a low cost. Therefore, the author and others tried to manufacture a nano composite material by the conventional powder metallurgical method, and found it possible to make nano composites with many composites, such as  $\text{Al}_2\text{O}_3/\text{SiC}$ ,  $\text{Al}_2\text{O}_3/\text{Si}_3\text{N}_4$ ,  $\text{MgO}/\text{SiC}$ ,  $\text{Al}_2\text{O}_3/\text{TiC}$ ,  $\text{Y}_2\text{O}_3/\text{SiC}$ , natural mullite/ $\text{SiC}$ ,  $\text{B}_4\text{C}/\text{SiC}$ , and  $\text{Si}_3\text{N}_4/\text{SiC}$ . Initially, it was possible to make these nano composite materials only by the hot press method, but now they can be made by atmospheric sintering/hot isostatic pressing (HIP) combination or simple atmospheric sintering.

As a result of research on the nano composite process with the use of an electron microscope, it was found that conditions for the fabrication of nano

composites by the sintering method are different from those for solid-phase and liquid-phase sintering. The following points are important for solid-phase sintering.

- a) The matrix powder grain diameter should be 100~500 nanometers (nm).
- b) Powder with a grain diameter of 200 nm or less should be selected as nano grains to serve as the disperse phase.
- c) These powders should be disperse-mixed uniformly.
- d) Sintering conditions should be selected to ensure that grains will grow in the matrix phase but not in the disperse phase.

It should be noted that all second phases should not necessarily be taken into grains when an in-grain nano composite material is made by sintering, and that part of them can be dispersed in grain boundaries as long as they do not hamper the role of nano grains dispersed inside the grains. For example, in the case of an  $\text{Al}_2\text{O}_3/\text{SiC}$  nano composite, SiC with an average grain diameter of some 200 nm can be chosen as the second phase.

In the case of liquid-phase sintering with  $\text{Si}_3\text{N}_4$  as the matrix, the following conditions are important.

- a) Powder with a grain diameter of 100 nm or less should be selected as nano grains for the disperse phase.
- b) The two powders should be mixed uniformly.
- c) The disperse phase should not be dissolved in the liquid phase deriving from the sintering aid (selection of the disperse phase, sintering aid and sintering conditions).
- d) The disperse phase should become the core with  $\beta\text{-Si}_3\text{N}_4$  phase deposits again from the liquid phase.

In this sintering mechanism, the disperse phase serves as the growth core of the matrix. Thus, it goes without saying that the second phase dimensional shape and uniform dispersion conditions are stricter than those of solid-phase sintering. As noted later, in-grain nano grains introduce local residual stress inside the matrix grains. Since grain boundary dispersed nano grains control the grain boundary structure, it is important to choose composite systems and sintering conditions that will not cause any chemical reactions in any sintering mechanism in order to ensure achievement of the nano composite effect.

### 3. Nano Composite Effect

Figure 3 shows the relationship, between the amount of SiC and the destruction strength of an  $\text{Al}_2\text{O}_3/\text{SiC}$  in-grain nano composite material. This composite material can be made by uniformly mixing an  $\text{Al}_2\text{O}_3$  powder (average secondary

grain diameter: 400 nm, average primary grain diameter: 20 nm) and an SiC powder (average primary grain diameter: 50 nm) with a ball mill, and hot press-sintering the mixture at 1,500–1,800°C. This manufacturing process looks very rough, but as transmission electron microscope (TEM) photographs of the  $\text{Al}_2\text{O}_3$ /17%SiC nano composite material (Figure 3) show, fine SiC grains were in fact uniformly dispersed in the close  $\text{Al}_2\text{O}_3$  matrix, mostly within  $\text{Al}_2\text{O}_3$  grains.

As is clear from the high-resolution TEM image shown in Figure 4, no reaction phase existed in the  $\text{Al}_2\text{O}_3$ -SiC interface, and a well-matched interface was achieved. As a result, dispersing SiC grains at a rate of about 5 vol% improved fracture toughness by some 50 percent, and fracture strength by more than fourfold to attain a combined strength of 1,500 MPa or more. The strength of a MgO/SiC nano composite material manufactured by sintering with a hot press a uniform mixture of MgO powder with an average grain diameter of some 100 nm and SiC powder with a primary average grain diameter of 50 nm was about twice that of the MgO single phase, and its toughness was about five times as great, as shown in Table 1. Further, the use of a nano composite remarkably curtails unevenness in strength as shown in Figure 5.



Figure 4. TEM Photograph of  $\text{Al}_2\text{O}_3$ /SiC Nano Composite

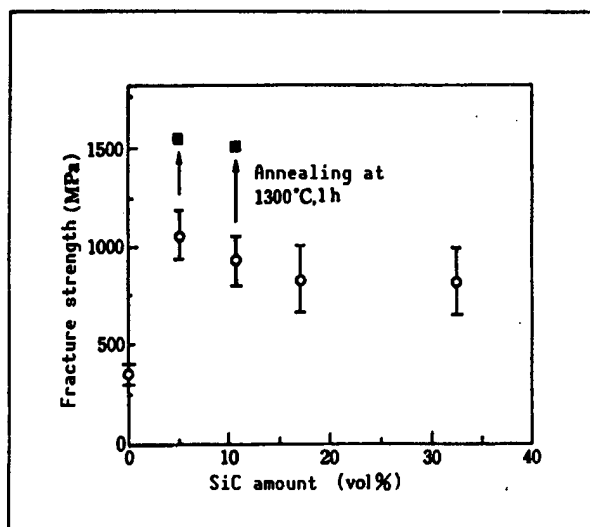


Figure 3. Strength of  $\text{Al}_2\text{O}_3$ /SiC Nano Composite

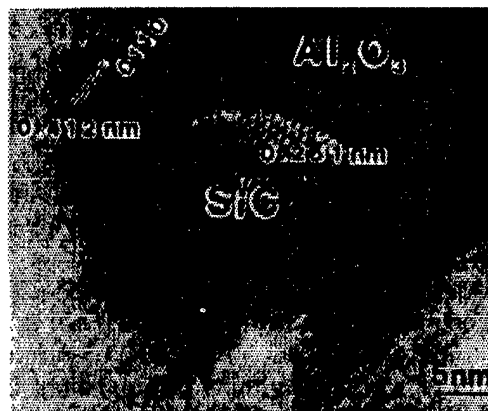


Figure 5. High-Resolution TEM Photograph of SiC Nano Grain Inside  $\text{Al}_2\text{O}_3$ /SiC Nano Composite

Figure 6 shows the high-temperature strength of  $\text{Al}_2\text{O}_3$ /SiC and MgO/SiC nano composite materials. Nano composites sharply reduce the decline in strength at high temperatures. The strength of  $\text{Al}_2\text{O}_3$  at 1,000°C was similar to that at room temperature, and the strength of MgO did not fall until the temperature

Table 1. Improvement in Mechanical Characteristics of Ceramics by Nano Composite

Composite materials	Toughness (MPam <sup>1/2</sup> )	Strength (MPa)	Maximum temperature (°C)
Al <sub>2</sub> O <sub>3</sub> /SiC	3.5→4.8	350→1520	800→1200
Al <sub>2</sub> O <sub>3</sub> /Si <sub>3</sub> N <sub>4</sub>	3.5→4.7	350→850	800→1300
MgO/SiC	1.2→4.5	340→700	600→1400
Mullite/SiC	1.2→3.5	150→700	700→1200
Si <sub>3</sub> N <sub>4</sub> /SiC	4.5→7.5	850→1550	1200→1400

reached 1,400°C. Both of these represent an extraordinary improvement. It also became clear that the use of nano composites greatly improves high-temperature hardness, and resistance to thermal shock, fatigue, and creep destruction.

As can be clearly seen from Table 1, a dramatic improvement in mechanical characteristics caused by dispersed nano grains also was observed in other nano composites, including Al<sub>2</sub>O<sub>3</sub>/TiC and mullite/SiC. This is apparently because dispersed nano grains play the following roles.

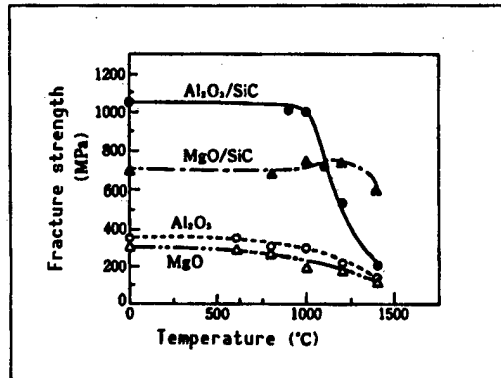


Figure 7. High-Temperature Strength of Al<sub>2</sub>O<sub>3</sub>/SiC, MgO/SiC Nano Composites

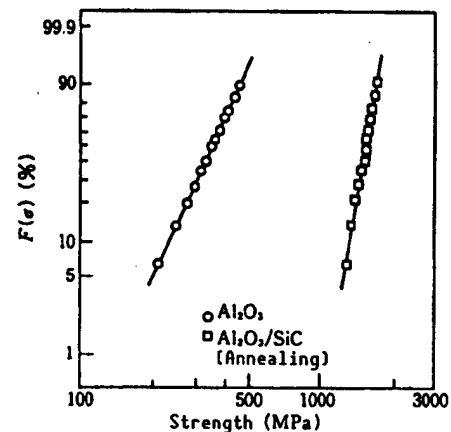


Figure 6. Weibull Plot of Strength of Al<sub>2</sub>O<sub>3</sub>/SiC Nano Composite

(1) Local stress arising from nano grains generates subgrain boundaries, as shown in Figure 7, at a high temperature that allows the matrix to undergo plastic deformation during cooling from the manufacturing temperature, and achieves nano-level miniaturization of the structure to attain high strength and high reliability. The improved strength of the Al<sub>2</sub>O<sub>3</sub>/SiC nano composite shown in Figure 2 after annealing for about an hour at 1,000~1,300°C is because the subgrain boundaries grow farther due to annealing as shown in Figure 8.

(2) Nano grains cause the front end of a crack to deviate, thereby increasing fracture toughness.

(3) Residual tensile stress generated around nano grains induces fractures inside grains to improve high-temperature strength.

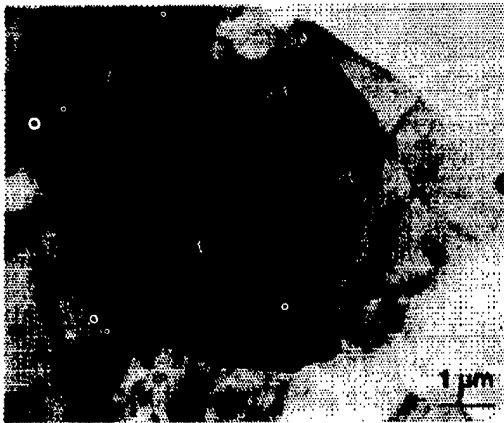


Figure 8. Subboundary Inside  $\text{Al}_2\text{O}_3$  of  $\text{Al}_2\text{O}_3/\text{SiC}$  Nano Composite



Figure 9. Subboundary in  $\text{Al}_2\text{O}_3/\text{SiC}$  Nano Composite Developed by Annealing

(4) Because nano grains pin the moves of dislocations, a drop in hardness at high temperatures improves resistance to creep fracture, thereby curbing deformation at high temperatures.

An  $\text{Si}_3\text{N}_4/\text{SiC}$  nano composite material can be manufactured by subjecting to either hot pressing or atmospheric sintering an amorphous Si-C-N composite precursor powder synthesized by CVD of  $[\text{Si}(\text{CH}_3)_2\text{NH}] + \text{NH}_3 + \text{H}_2$ . As Table 1 and Figure 9 show, this system shows the most remarkable characteristic improvement. But unlike oxide systems, dispersed nano grains of this system play the following roles.

(1) As explained above, SiC inside grains serves as the core for growth at the time of  $\beta\text{-Si}_3\text{N}_4$  grain deposition, developing a columnar structure and improving strength and toughness.

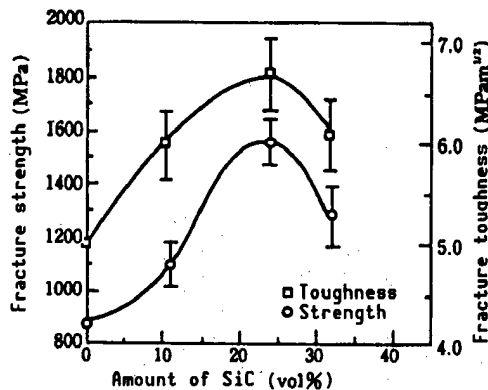


Figure 10. SiC Dispersion Effect on  $\text{Si}_3\text{N}_4/\text{SiC}$  Nano Composite

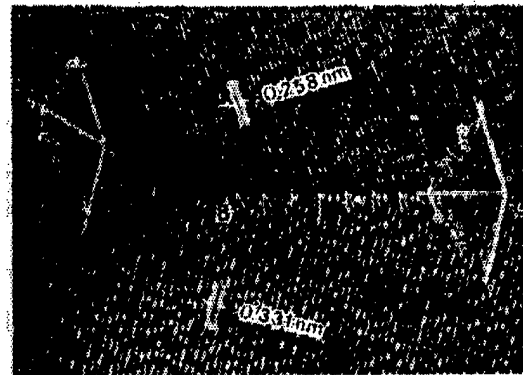


Figure 11. SiC-Matrix Interface in Grain Boundary of  $\text{Si}_3\text{N}_4/\text{SiC}$  Nano Composite

(2) SiC grains dispersed in the grain boundaries directly couple with  $\text{Si}_3\text{N}_4$  in the matrix, as shown in Figure 10 curb slips in grain boundaries, together with the generation and coupling of



cavities, serves to improve mechanical characteristics at high temperatures, as shown in Figure 11.

(3) An increase in the number of dispersed SiC grains leads to the miniaturization of  $\text{Si}_3\text{N}_4$  grains.

#### 4. Addition of New Functions by Nano Composite

When the production of a nano composite material (nano/nano composite) whose structure is sharply miniaturized by increasing the amount of SiC and by intentionally leaving about 35 percent of the  $\alpha\text{-Si}_3\text{N}_4$  intact by adjusting sintering conditions, and unlike the above-mentioned  $\beta\text{-Si}_3\text{N}_4/\text{SiC}$  nano composite material sintered at 1,750~1,800°C to ensure high strength at high temperatures, it is possible to add a superplastic deformation capability to  $\text{Si}_3\text{N}_4$  ceramics as predicted in the previous chapter (Figure 12). It should be noted that, unlike metals, a change occurs in the fine structure during superplastic deformation, and, after the deformation, the structure turns into a nano composite structure that has a high level of strength up to high temperatures.

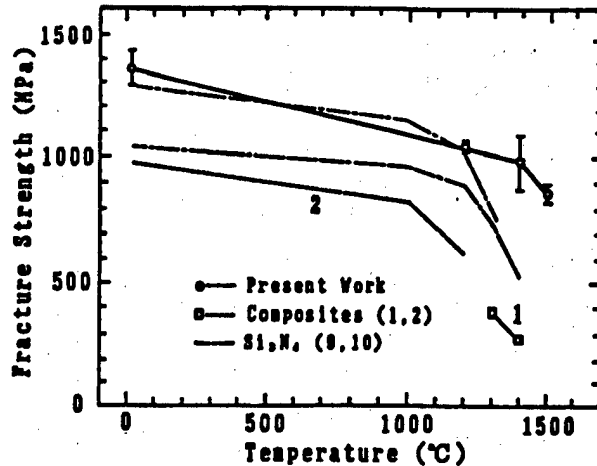


Figure 12. Improvement in High-Temperature Strength of  $\text{Si}_3\text{N}_4/\text{SiC}$  Nano Composite

It is possible to manufacture a grain boundary nano composite material with nano-level amorphous SiC arranged in SiC grain boundaries by adding a polysilastyrene organic compound precursor—which turns into SiC when heated to a high temperature—to SiC powder, and then sintering the mixture at 1,600~1,900°C. The strength of this nano composite material is about 450 MPa at a high temperature of 1,500°C. Also, it maintains the characteristics of SiC, and has free-machining characteristics like metals, as shown in Figure 13. The free-machining characteristics of the SiC/amorphous SiC grain boundary nano composite material apparently have something to do with nano-size open holes and nano grains that exist in SiC grain boundaries.

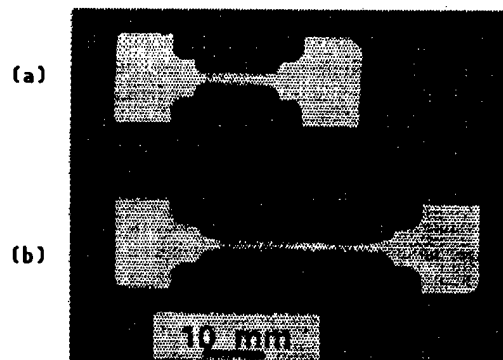


Figure 13. Superplastic Deformation of  $\text{Si}_3\text{N}_4/\text{SiC}$  Nano Composite (a) Before Deformation; (b) After Deformation

I would like to note that recent data show that the most basic physical characteristics directly controlled by chemical coupling, such as elasticity and thermal expansion, can be controlled by the use of a nano composite, regardless of holes and microcracks.

## 5. Micro/Nano Hybrid Materials

It has become clear that it is possible to improve the mechanical characteristics of various ceramics dramatically through the use of a nano composite. Compared to metallic materials, however, even the improved fracture toughness is still insufficient. But this problem can be solved by further reinforcing the nano composite material with long staples, as is clear from data on the long staple-reinforced SiAlON/SiC nano composite material shown in Table 2. The room temperature strength and toughness achieved by this material are superior to those of carbide materials (WC/Co cermet) widely used in industrialized societies. There have been no reports on the development of a material whose mechanical characteristics do not deteriorate at temperatures above 1,300°C, but rather improve at high temperatures.




Figure 14. Example of Processing by Milling Machine of SiC/SiC Grain Boundary Nano Composite

Table 2. Mechanical Characteristics of Carbon Fiber-Reinforced SiAlON/SiC Nano Composite

Composites	Strength (MPa)			Toughness (MPam <sup>1/2</sup> )	
	RT	1,300°C	1,500°C	RT	1,300°C
Long fiber-reinforced SiAlON	314			9.5	
Long fiber-reinforced SiAlON/SiC nano composite	705	1,075	790	25.0	22.0

## 6. Conclusion

We succeeded in manufacturing the three new kinds of nano composite materials—in-grain, grain boundary, and nano/nano composite materials—using the conventional sintering method, and we studied the relationship between the nano structure and various mechanical characteristics. Major nano composite effects can be summed up as follows.

1) In the case of oxide-based ceramics, strength and toughness can be improved from two to five times by dispersing the nano-size second phase, which has a smaller thermal expansion rate, inside the grains of the matrix. This technology also can be used to improve various mechanical characteristics at high temperatures dramatically.

2) The improvement in strength and toughness can be explained as follows: Residual stress stemming from a difference in thermal expansion rates between nano grains and the matrix, accumulated during cooling of the material from

the manufacturing temperature, generates dislocations in a high-temperature range where the matrix still can undergo plastic deformation. The dislocations are pinned by already hard dispersed nano grains, generating a subboundary, and this divides the matrix into smaller grains. The improvement in various mechanical characteristics at high temperatures apparently occurs because of curbs on deformation at high temperatures by nano grains.

3) As for  $\text{Si}_3\text{N}_4$ , a typical nonoxide ceramic, it became clear that it is possible to improve various mechanical characteristics sharply by dispersing nano-size SiC grains, for example, inside grains and grain boundaries. But unlike oxide-based ceramics, SiC grains dispersed inside grains foster the growth of the matrix's  $\text{Si}_3\text{N}_4$  grains into bars. SiC grains dispersed inside grain boundaries eliminate the impurity phase generated in grain boundaries by the sintering aid, and directly couple with the matrix's  $\text{Si}_3\text{N}_4$  grains. This serves to curb slips of grain boundaries, which occur at high temperatures, and SCG caused by the generation and coupling of cavities, thereby serving to improve various mechanical characteristics at high temperatures dramatically.

4) Nano-nano composite and grain boundary nano composite materials provide new mechanical functions, such as free-machining characteristics seen in metals, and superplastic deformation.

5) The manufacture of superstrong and supertough ceramics is possible with a micro/nano combination. The most promising method is to reinforce a grain boundary nano composite material with long staples.

## Development of Metal Matrix Composite Materials

936C3802B Tokyo SENTAN FUKUGO ZAIRYO SEMINA in Japanese 14-15 Jul 92 pp 18-21

[Article by Taketami Yamamura, Ube Industries, Ltd.]

[Text] Metal Matrix Composites (MMCs)

As lightweight heat-resistant materials for use in the aerospace field, polyimide resin and other heat-resistant resin composite materials have good specific strength and specific rigidity at temperatures up to 570 K. But at higher temperatures, MMCs with a highly heat-resistant matrix enjoy certain advantages. As Figure A shows, MMCs are based on, beginning with the lower temperature side, heat-resistant aluminum, titanium, titanium-aluminum intermetallic compounds, super alloys (including nickel-aluminum intermetallic compounds) and high-melting point metals (including high-melting point intermetallic compounds).

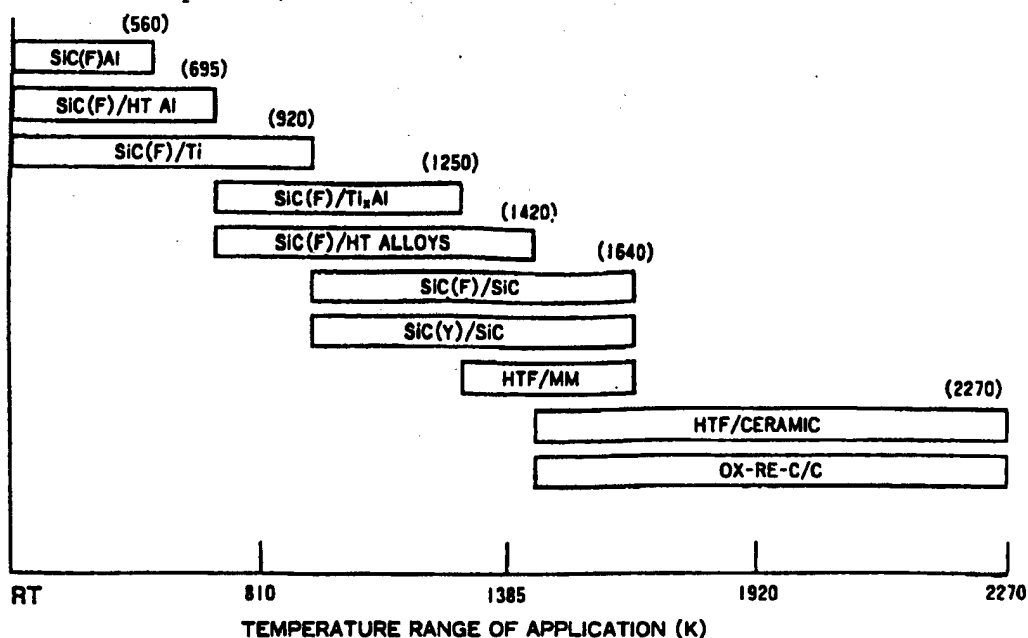


Figure A. Temperature Range of Application of MMCs and Other Composites

## (1) Aluminum-Based MMC

Aluminum-based MMCs are the most researched MMCs, but only a few research reports have been made on heat-resistant aluminum MMCs. Figure B shows the relationship between temperature and the specific strength of MMCs developed under the auspices of the next-generation project. SiC<sub>CVD</sub> fiber/heat-resistant aluminum SCS-2/Al-4Ti and SCS-2/Al-8Cr-1Fe have an excellent high-temperature strength similar to that of Ti-alloy MMC reinforced with SiC fibers (SCS-6), and their specific strength is remarkably high at 55 km or higher at 700 K.

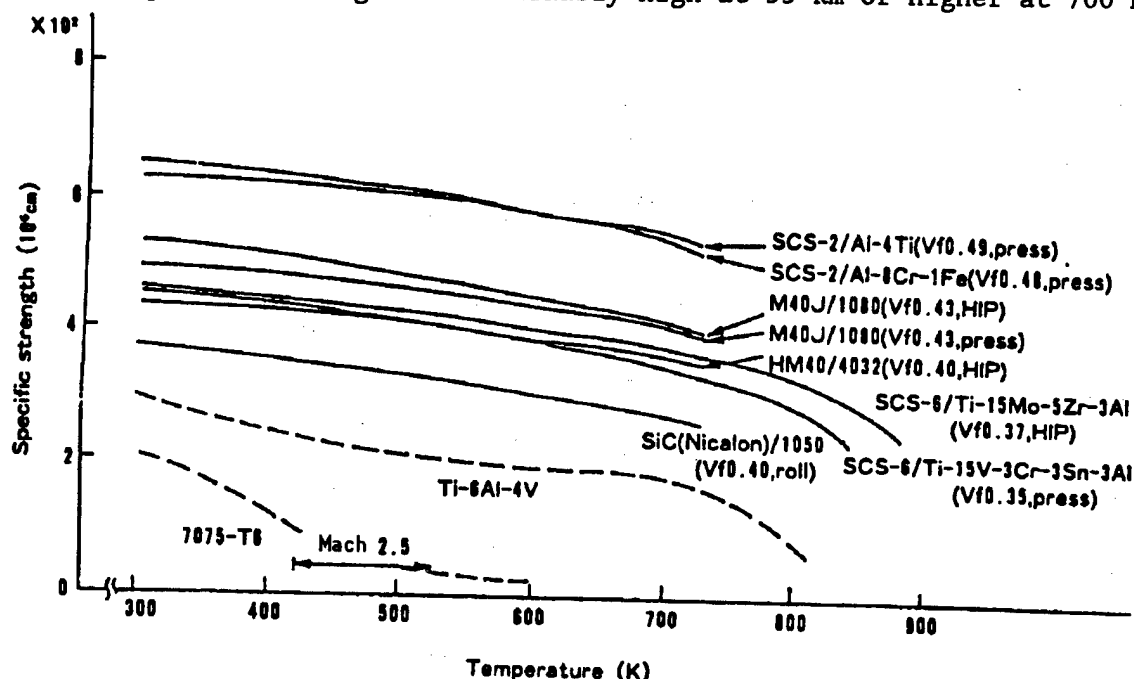


Figure B. Relationship Between Temperature and Specific Strength of MMCs Developed Under the Next-Generation Project

As for precursor-type Si-C-O fibers (Nicalon) and Si-Ti-C-O fibers (Tyranno fiber), heat-resistant aluminum MMCs have been developed. Both use an Al-Al<sub>3</sub>Ni eutectic crystal alloy as the matrix (Nicalon/Al-5.7Ni, Tyranno/Al-8Ni). Their strength is lower than that of SiC<sub>CVD</sub> MMCs, but they are highly heat resistant, maintaining their room temperature strength up to around 700 K. These MMCs are unidirectional, and their strength in the 90° direction is higher than that of other Al-based MMCs.

## (2) Titanium- and Titanium-Aluminide-Based MMCs

Both titanium-based and titanium-aluminide-based MMCs are reinforced by SiC fibers by chemical vapor deposition (SiC<sub>CVD</sub>). The mainstay is SiC-6, whose fiber surface layer is coated with a carbon-enriched film to promote a better matching of fibers and the matrix. As for titanium MMCs, the matrix alloy is shifting from Ti-6Al-4V to Ti-15V-3Cr-3Sn-3Al and Ti-10V-2Fe-3Al, both  $\beta$  alloys, to achieve better forming characteristics or greater strength. Hot pressing and hot isostatic pressing (HIP) of a foil/fiber/foil sandwich are

widely used, and have been technically established as the composite forming method, which is now entering the parts manufacturing technology development phase for application to actual machines. With regard to SiCS-6/titanium MMCs, it already has been confirmed that an interfacial reaction progresses when these materials are heated to 770 K or more. The reaction layer, which consists of carbides and silicides, becomes thicker, but it has a smaller-than-expected influence on tensile strength. However, the problem of oxidation by heating in the atmosphere is pointed out. Table A shows the characteristics of SCS-6/Ti-6Al-4V and SCS-6/Ti-15V-3Cr-3Sn-3Al.

Table A. Data on Characteristics of SCS-6/Ti Alloy (Sample dimensions-62-layer panel)

Mechanical characteristics of SiC/Ti-6-4 (35 v/o)				
Before heat treatment			After heat treatment (7 hours, 905°C)	
	X	S.D.	X	S.D.
Tensile strength reached MPa (kgf/mm <sup>2</sup> )	1690 (172)	119.3(12.1)	1434 (146)	108.9 (11.1)
Elasticity GPa (tonf/mm <sup>2</sup> )	186.2 (18.9)	7.58 (0.8)	190.3(19.4)	8.3 (0.9)
Distortion	0.96	0.091	0.86	0.087
Mechanical characteristics of SiC/Ti-15-3-3-3 (38-41 v/o)				
Before heat treatment			After heat treatment (16 hours, 480°C)	
	X	S.D.	X	S.D.
Tensile strength reached MPa (kgf/mm <sup>2</sup> )	1572 (160)	138 (14)	1951 (198)	96.5 (9.8)
Elasticity GPa (tonf/mm <sup>2</sup> )	197.9 (20.1)	6.21 (0.7)	213.0(21.7)	4.83 (0.5)
Distortion	—	—	—	—

As for titanium-aluminide MMCs, research on Ti<sub>3</sub>Al( $\alpha$ -2) and TiAl( $\gamma$ ) as the matrix is under way. These MMCs are taken up under the next-generation project "Advanced Materials With Superhigh Resistance to Severe Environments" sponsored by the Ministry of International Trade and Industry. Development work using Nicalon and Tyranno started in FY 1989. The alloys themselves can resist temperatures of 1,090 K and 1,250 K, respectively. MMC research also is focusing on Ti<sub>3</sub>Al alloys, for which alloy research is well under way. Ti-24Al-11Nb, Ti-25Al-13Nb, Ti-25Al-17Nb, and Ti-25Al-10Nb-3V-1Mo are used as matrix alloys. Plasma spraying is attracting attention as a preforming composite forming method. The fiber/matrix interface reaction of SCS-6/Ti<sub>3</sub>Al is the

subject of a number of research efforts, little information on its mechanical properties is available. At the time of SCS-6/Ti3Al forming, the interface reaction generates a reaction layer made of carbides and silicides. As a result, a  $\beta$ -depleted area is formed in the region adjacent to the matrix, and this region becomes hardened, causing a drop in ductility, which in turn leads to a deterioration in the composite's strength.

### (3) Superalloy and Nickel-Aluminide MMCs

Research on a tungsten fiber-reinforced superalloy for application to jet engine turbine blades has started in the United States. Improving the tungsten fibers, research on matching matrix alloys, composite technology development, and creep characteristics evaluation all have been conducted. It is said that the temperature resistance of widely used superalloys needs to be improved by about 50 K, but this has yet to be achieved for practical purposes.

Research on nickel-aluminide MMCs also is under way, using SCS-6 and  $B_4C/B$  fibers. But the interface reaction is pronounced in both of these, and some kind of barrier coating is necessary. Given these circumstances, research is still restricted to a preliminary study on matching between the matrix and reinforcing fibers.

## **Tyranno Fiber-Reinforced Composite Materials**

936C3802C Tokyo SENTAN FUKUGO ZAIRYO SEMINA in Japanese 14-15 Jul 92 pp 22-28

[Article by Yoshiharu Waku and Taketami Yamamura, Ube Industries, Ltd.]

[Text] It is said that the advent of materials that offer a new function makes technical innovation possible, and new materials have become an indispensable factor in the development of high technology. Composites—along with ceramics, semiconductor materials, and superconducting materials—are attracting attention as new materials that have both technical and social impacts.

Against the backdrop of increasing practical applications of fiber-reinforced plastics (FRP) that use glass, carbon, Aramide, or boron fibers as reinforcers, there is an increasing demand for materials with excellent high-temperature characteristics and heat stability in spacecraft and aircraft, and in high-efficiency turbines. Fiber-reinforced metallic composite materials (FRM) are attracting attention as lightweight structural materials that have greater heat resistance than FRP. Reinforcers used in FRM include, besides the above-mentioned carbon and boron fibers, the more recently developed  $\text{Al}_2\text{O}_3$  fiber (E.I. duPont, Sumitomo Chemical, and 3M) which offers good heat resistance, a SiC/C composite fiber (AVCO), and a SiC fiber (invented by the late Professor Yajima of Tohoku University). These materials can be used as staples and fibers. There are also various whiskers, including SiC and  $\text{Si}_3\text{N}_4$ , and research is under way in various fields on FRM using these fibers as reinforcers.

It is necessary to devise a fiber layout that fully utilizes composite effects and anisotropy in order to develop high-strength and high-performance FRM. Fibers are required to have excellent heat resistance and mechanical characteristics, as well as ease of secondary processing, such as woven cloth and three-dimensional textiles.

The most common matrix metals for FRM are various aluminum alloys. The fibers mentioned above are not necessarily sufficient in terms of their matching with matrix aluminum, heat resistance, and secondary processing into woven cloth or three-dimensional textiles. For these reasons, it will be necessary to improve them or to develop new, more capable inorganic long fibers.



the authors had others are now developing a Si-Ti-C-O-based inorganic long fiber (Tyranno fiber®), aiming at realizing a high-performance fiber suitable for use in various composite materials, high heat-resistant materials, and FRM. Here, we will discuss the manufacturing method for the Tyranno fiber and the fiber's characteristics, matching with aluminum, FRM manufacturing method, characteristics of Tyranno-reinforced aluminum and its potential uses.

#### Tyranno Fiber Manufacturing Method and Characteristics

The Tyranno fiber is manufactured by melt-spinning polytitanocarbosilane, making the spun fiber infusible, and sintering it. The process to make it infusible is a heating process conducted at a temperature of 200°C or less in the atmosphere in order to prevent the fiber from losing its shape during sintering. It makes the spun fiber infusible with bridging by oxygen in the air. Sintering is done by continuously processing the infusible fiber at 1,000~1,500°C in nitrogen.

Table 1. Characteristics of Tyranno Fiber

Fiber diameter	8~12 $\mu\text{m}$
Filament count/yarn	200·n (n = 1~8)
Density (at 25°C)	2.3~2.4 g/cm <sup>2</sup>
Tensile strength	2.8~3.0 GPa
Tensile elasticity	200~220 GPa
Fracture extension	1.4~1.5
Thermal expansion coefficient (fiber axis direction, 0~500°C)	$3.1 \times 10^{-6}/^{\circ}\text{C}$
Specific heat	0.19 cal/deg·g (330°C) 0.28 cal/deg·g (670°C)

Table 1 shows the Tyranno fiber's characteristics. The Tyranno fiber consisting of Si, Ti, C, and O maintains an amorphous structure up to a high temperature of 1,400°C. The fiber diameter can freely be controlled above 8  $\mu\text{m}$ , and unevenness can be curbed up to  $\pm 1.5 \mu\text{m}$ . The fiber's tensile strength and tensile elasticity are 2.8~3.0 GPa and 200~220 GPa, respectively. It not only has good mechanical characteristics, but has a small density of 2.3~2.4 g/cm<sup>2</sup>, making it suitable as a reinforcer for lightweight composites. Its thermal expansion coefficient is small at  $3.1 \times 10^{-6}/^{\circ}\text{C}$ , and there is little difference in the coefficient between the fiber's axis and diameter directions. As the table shows, it has a fracture extension of 1.4~1.5 percent, which is larger than conventional inorganic fibers, and its nodal strength is high. Because of these factors, the fiber can be processed into plain fabrics, Zhuzi fabrics, three-dimensional fabrics, and others.

## Matching Tyranno Fiber With Aluminum Matrix

In the development of fiber-reinforced metal (FRM), fiber deterioration due to reactions with the molten metal at the time of composite material manufacturing, improper metal-fiber wetting, and the uneven dispersion of fibers into the metal greatly hinders efforts to improve their performance. Figure 1 shows the influence of soaking time on the tensile strength deterioration of Tyranno and SiC fibers when the fibers are soaked in pure molten aluminum (1070) or 6061 alloy (670°C). Even the SiC fiber, which is said to have better FRM matching than other inorganic fibers, suffers a steep drop in strength when soaked even for a short time. In contrast, the strength of Tyranno fiber is little diminished in molten aluminum, and there is no need for surface treatment, thus making various FRM manufacturing methods available.

Deterioration of the Tyranno fiber can be reduced further by increasing the amount of Ti in the fiber. The strength deterioration in molten aluminum of both Tyranno and SiC fibers has something to do with carbon and oxygen that exist nonstoichiometrically in the fibers. The smaller decline in the strength of the Tyranno fiber presumably is due to an increase in the coupling force among elements constituting the fiber (Si, Ti, O, and C) caused by the addition of Ti.

## Manufacturing Method for Tyranno Fiber-Reinforced Aluminum Composite Materials

As the Tyranno fiber matches well with aluminum, Tyranno fiber-reinforced aluminum composite materials can be manufactured by various FRM manufacturing methods. For complex shapes and small objects the authors adopt the squeeze-casting method for its ability to make near net shapes and its suitability for low cost mass production. For large objects, we use plasma spray preimpregnation diffusion bonding. In either method, the performance of the FRM depends greatly on manufacturing process factors, such as fiber-matrix metal interfacial matching (bonding and reactivity), orientation and uniform dispersion of fibers, fiber damage during manufacturing, and composite material matrix casting defects.

### 1. Squeeze Casting

This method makes it possible to obtain a material with almost no vesicles, depending on manufacturing conditions, and a relatively uniform dispersion of reinforcing fibers in the composite material. Forming a near net shape is possible without secondary processing, and the method is characterized by volume production capability and low manufacturing cost. Figure 2 shows the

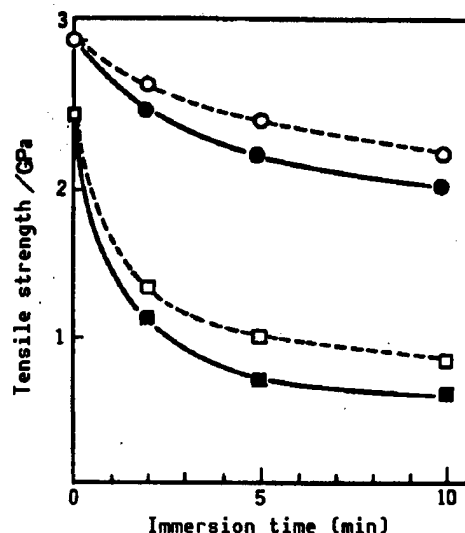


Figure 1. Drop in Strength of Tyranno Fiber ( $\bullet, \circ$ ), SiC Fiber ( $\blacksquare, \square$ ) as a Function of Time of Immersion in Pure Aluminum (Broken Line), 6061 Alloy (Solid Line)

FRM manufacturing process based on the squeeze casting method. A preform preheated to a certain temperature is installed within a metal mold kept at a certain temperature. After closing the mold, molten aluminum is injected into the preform by a plunger to manufacture the FRM. Photo 1 shows the structure of Tyranno fiber-reinforced aluminum made by this method. It uses a Tyranno fiber that has a SiC powder on its surface (jointly developed with Toyoda Chuo Kenkyusho). As the photo shows, the Tyranno fibers are uniformly dispersed, and there is no contact between fibers, resulting in a high-performance FRM.

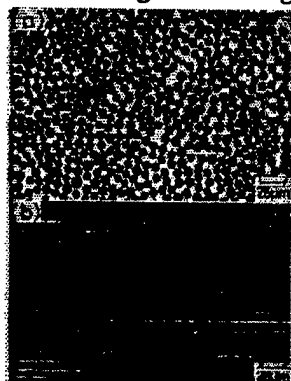


Photo 1. Cross-Sectional Structure of Tyranno Fiber-Reinforced Al Made by Squeeze Casting

methods makes it possible to achieve uniform fiber dispersion for production of a good plasma-spray prepreg sheet with the matrix metal fully impregnated among the fibers.

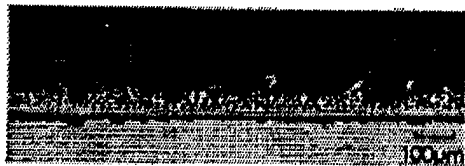


Photo 2. Cross-Sectional Structure of Plasma-Spray Tyranno Fiber Prepreg Sheet

Photo 2 shows a cross sectional structure of a prepreg sheet made by plasma-spraying pure aluminum onto Tyranno fibers. It shows that the Tyranno fibers are uniformly dispersed. Photo 3 shows the cross sectional structure of an FRM made by laminating the prepreg sheets and hot pressing them.

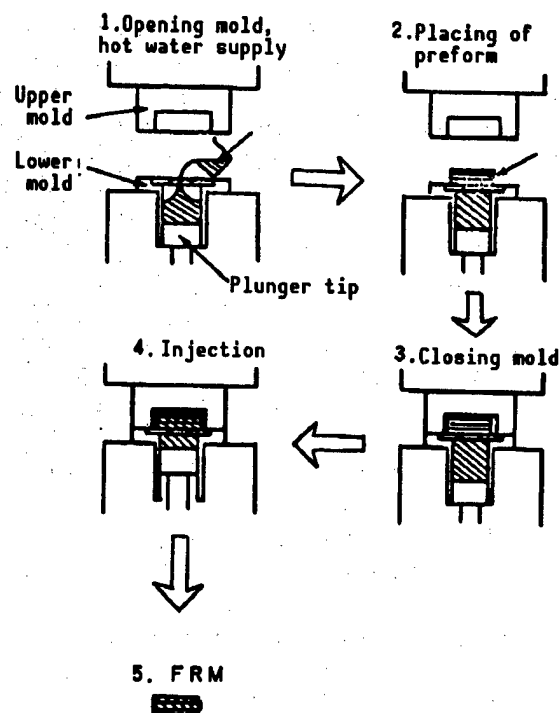


Figure 2. FRM Manufacturing Process Using Squeeze Casting

## 2. Manufacturing Plasma-Spray Prepreg Sheet

Prepreg sheet manufacturing by plasma spraying is generally used for fibers with large diameters of 100~150  $\mu\text{m}$ , such as SiC/C composite fiber produced by chemical vapor deposition (CVD). It is not often used for fibers with small diameters of 8~20  $\mu\text{m}$ , because it is difficult to impregnate the matrix metal among small fibers by plasma spraying. But improving the fiber opening and spraying

## Characteristics of Tyranno Fiber-Reinforced Aluminum Composite Materials

### 1. Typical Mechanical Characteristics

Typical mechanical characteristics at room temperature of a Tyranno fiber-reinforced pure aluminum composite material are shown in Table 2. Both tensile strength and flexural strength are good. Flexural strength in a direction at right angles to the fibers (T direction) is particularly high at 40~50 MPa. The Tyranno fiber-reinforced aluminum's T-direction mechanical characteristics are very good, given a flexural strength of 40~50 MPa for the M40/Al alloy reinforced by high-flexibility carbon fibers (M40), and 90~190 MPa for other inorganic fiber-reinforced aluminum materials.

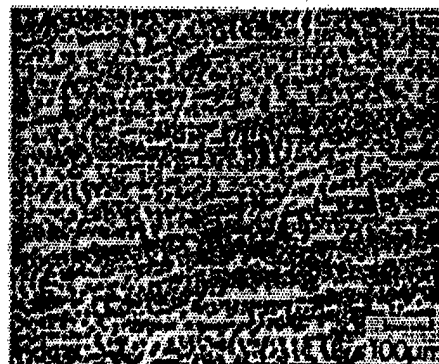


Photo 3. Cross-Sectional Structure of FRM Made by Plasma-Spray Prepreg Hot Press

Table 2. Typical Mechanical Characteristics of Tyranno Fiber-Reinforced Aluminum

Mechanical characteristics	
Tensile strength	1,100~1,200 MPa
Tensile elasticity	98~108 GPa
Flexural strength (L direction) (T direction)	1,450~1,550 MPa 320~340 MPa
Rotating flexural fatigue strength	370 MPa
Impact value *1 (U-notch)	316 J/m <sup>2</sup>
Hardness H <sub>8</sub> *2 (0°) (90°)	163 90

Metallic composite materials reinforced by long fibers are generally strong in the fiber direction, but weak in a direction right angles to the fibers. This is because the interfacial coupling force of reinforcing fibers and the matrix is weak, and fracture generates from the interface. But a dimple pattern, which indicates ductile fracturing of the material, can be seen in a scanning electron microscope (SEM) picture of the T-direction flexural fracture surface of Tyranno fiber-reinforced aluminum, as shown in Photo 4. This means that the fracture is generated in the matrix, not the interface between the Tyranno fibers and the matrix. This is because the Tyranno fiber matches very well with aluminum.

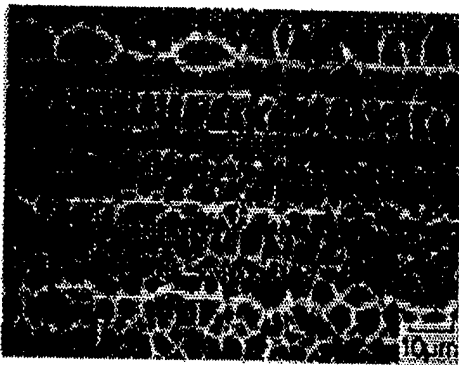


Photo 4. SEM Photo of T-Direction Flexural Fracture Surface of Tyranno Fiber-Reinforced Aluminum

## 2. High-Temperature Flexural Strength

Figure 3 shows the effect of temperature on Tyranno fiber-reinforced aluminum. For comparison, it also shows that of the 6061-T6 aluminum alloy, which is used as a general structural material. The flexural strength of the 6061-T6 alloy drops from around 423 K (150°C), but the Tyranno FRM maintains a flexural strength of 1.1 GPa at 623 K (350°C) and 0.7 GPa even at 673 K (400°C).

Figure 4 shows the relationship at room temperature between flexural strength and heating time after the Tyranno FRM was kept at 623 K (350°C) for 400 hours (1.44 Ms). A slight decline in strength is seen in the heating time range of 0-100 hours (0.36 Ms), but its strength remains constant for longer heating times. Measurement of the tensile strength of the Tyranno fiber extracted from the Tyranno FRM after the heating experiment also shows little deterioration of the fiber during heating. From these results, it is possible to say that the Tyranno FRM is thermally stable even at a high temperature of 623 K. A slight decline in strength in the initial heating stage is probably because dislocations already introduced at the time of casting were mended by heating and disappeared.

## 3. Impact Value

Figure 5 shows a load-displacement curve measured by an instrumental Charpy impact tester. The figure indicates that at room temperature (293 K), most of the absorbed energy is spent on generating a crack. At a high temperature

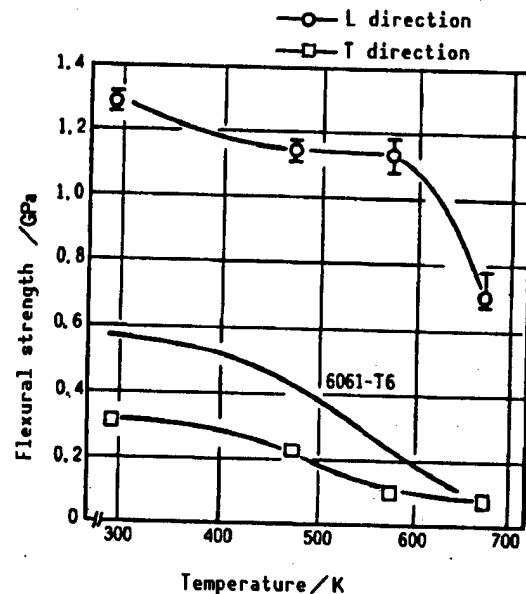


Figure 3. Effect of Temperature on the Flexural Strength of Tyranno Fiber-Reinforced Al

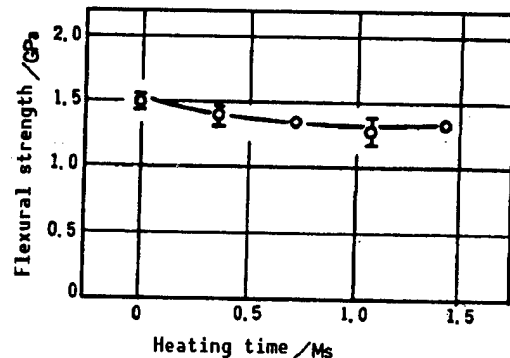


Figure 4. Relationship Between Flexural Strength and Heating Time of Tyranno Fiber-Reinforced Aluminum at 623 K

(573 K), the energy spent on developing a crack becomes larger than at room temperature, and the amount of absorbed energy itself gets larger. The relationship between the amount of absorbed energy and temperature is shown in Figure 6.

#### 4. Tyranno Fiber-Reinforced Aluminum Alloy

Table 3 shows the mechanical characteristics of the 6061, Al-Ni, Al-Co, and Al-Ti alloys when they are reinforced by Tyranno fibers. Alloying further improves flexural strength in the T direction, and also increases L-direction flexural strength to more than 1,500 MPa.

#### 5. Thermal Expansion Coefficient

Table 4 shows the thermal expansion coefficients of the Tyranno FRM. The coefficients in the fiber direction are close to the Tyranno fiber's thermal expansion coefficient of  $3.1 \times 10^{-6}/^{\circ}\text{C}$ . The coefficient in a direction at right angles to the fiber is  $20 \times 10^{-6}/^{\circ}\text{C}$ , close to  $25.6 \times 10^{-6}/^{\circ}\text{C}$  for pure aluminum.

#### 6. Specific Heat and Thermal Conductivity (See Table 5)

Specific heat tends to increase along with temperature, but there is no difference by fiber direction. Thermal conductivity in the fiber direction is about double the value in a direction at right angles to the fiber (T direction) and about half that of aluminum. This indicates that it has something to do with both the fiber's volume rate and direction.

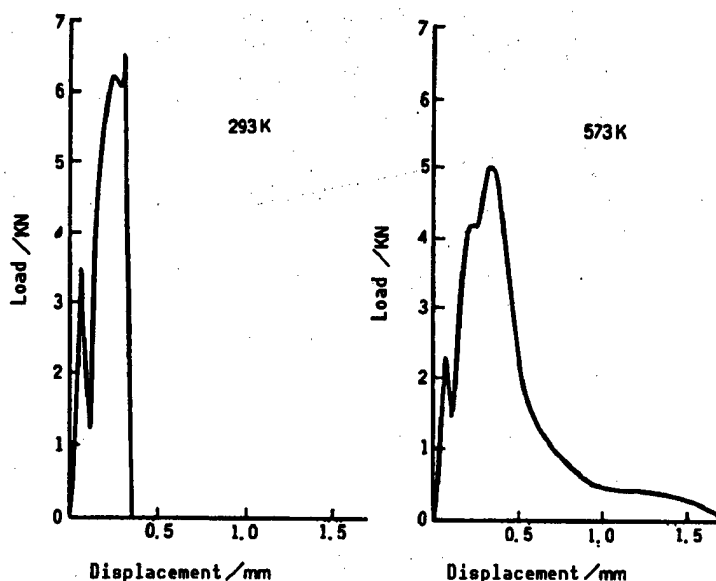


Figure 5. Load-Displacement Curve of Tyranno Fiber-Reinforced Aluminum in Impact Test

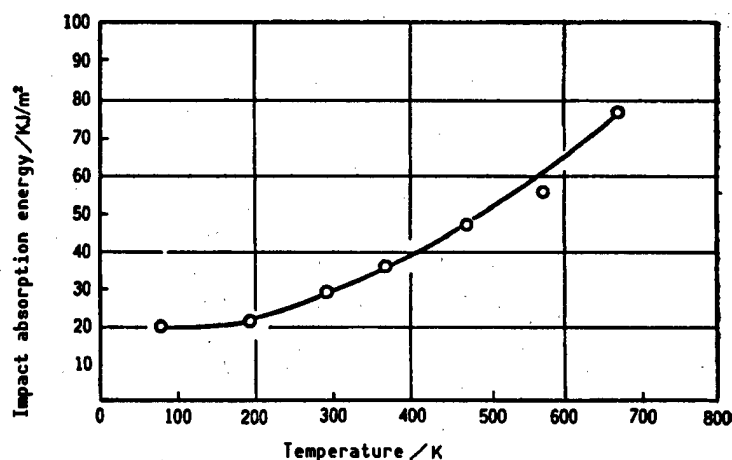


Figure 6. Effect of Temperature on Impact Absorption Energy of Tyranno Fiber-Reinforced Aluminum

Table 3. Mechanical Characteristics of Tyranno Fiber-Reinforced Aluminum

Alloy	Flexural strength	Flexural strength	
		L direction	T direction
6061 base FRM		1,000 MPa	370 MPa
Al-Ni base FRM		1,500 MPa	430 MPa
Al-Co base FRM		1,560 MPa	380 MPa
Al-Ti base FRM		1,480 MPa	250 MPa

Table 4. Thermal Expansion Coefficient of Tyranno Fiber-Reinforced Aluminum

Temperature (°C)	Thermal expansion coefficient $10^{-6}/^{\circ}\text{C}$	
	Fiber-longitudinal direction	Fiber-lateral direction
20~100	5.9	16.3
20~200	4.3	18.6
20~300	3.7	20.0
20~400	3.5	20.9
20~500	3.4	21.5
20~600	3.3	22.1

Table 5. Specific Heat and Thermal Conductivity of Tyranno Fiber-Reinforced Aluminum

	Temperature (°C)	Specific heat cal/g·°C	Thermal conductivity cal/cm·sec·°C
Fiber-longitudinal direction	25	0.20 <sub>4</sub>	0.22 <sub>8</sub>
	100	0.21 <sub>3</sub>	0.21 <sub>4</sub>
	200	0.22 <sub>4</sub>	0.21 <sub>0</sub>
	300	0.23 <sub>4</sub>	0.20 <sub>9</sub>
	400	0.24 <sub>4</sub>	0.20 <sub>7</sub>
	500	0.25 <sub>7</sub>	0.20 <sub>7</sub>
Fiber-lateral direction	25	0.20 <sub>9</sub>	0.12 <sub>6</sub>
	100	0.21 <sub>9</sub>	0.11 <sub>7</sub>
	200	0.23 <sub>2</sub>	0.11 <sub>9</sub>
	300	0.24 <sub>3</sub>	0.11 <sub>9</sub>
	400	0.25 <sub>5</sub>	0.12 <sub>0</sub>
	500	0.26 <sub>6</sub>	0.11 <sub>8</sub>

## Applications

Because Tyranno fiber-reinforced aluminum composite materials are light and have excellent mechanical characteristics both in the L and T directions, high heat resistance, and excellent fatigue characteristics, as explained above it is expected that they will be put to practical use in the aerospace, sports, and leisure fields.

Because there is little reaction between the Tyranno fiber and molten aluminum, it is possible to make FRM with squeeze casting, which has a low-cost mass production capability. It is also possible to manufacture near-net shape complex shapes. The application of this technology will make it possible to produce small automobile parts, such as connecting rods and pistons, and sporting goods out of FRM. Photo 5 [not reproduced] is an FRM piston head made by squeeze casting.

Tyranno fibers also are suitable for prepreg manufacturing with plasma spraying, and lamination and diffusion bonding of prepreg sheets make it possible to produce large formed objects. Plasma-sprayed prepreps are attracting keen interest in the aerospace sector.

The Tyranno fiber is a fiber that our company is developing as a new continuous fiber. The development of FRM using the fiber as the reinforcer has just started, and full-fledged development efforts have yet to be made. Most of the continuous inorganic fibers developed so far require some surface treatment to prevent reaction with matrix aluminum. But the Tyranno fiber is attracting attention as a fiber with the potential of being used with no surface treatment.

Aluminum alloys reinforced with the Tyranno fiber have a very high flexural strength on the order of 1,500 MPa in the fiber direction and 430 MPa in a direction at right angles to the fiber. As they also offer excellent heat resistance, abrasion resistance, and impact resistance, we believe they will steadily find practical applications in the aerospace, sports and leisure, and automotive fields. To that end, businesses have to improve fibers and to develop fibers with even higher levels of performance and low-cost composite technology; conduct basic and systematic research, including peripheral technologies; and make efforts to find practical applications.



## Development of SiC/SiC Matrix Composites

936C3802D Tokyo SENTAN FUKUGO ZAIRYO SEMINA in Japanese 14-15 Jul 92 pp 14-15

[Article by Hiroshi Ichikawa, Nippon Carbon Co.]

### [Excerpt] 1. Introduction

Amid the rapid progress of technological innovation, a number of major high-technology projects are under way around the world. These include space shuttles and space planes in the aerospace field, high-temperature gas reactors and nuclear fusion reactors in the atomic field, and high-temperature burning gas turbines in the energy field.

Structural materials for these technologies must have high levels of strength at high temperatures (1,200~2,000°C), high reliability (toughness, impact resistance, etc.) and environmental resistance (resistance to oxidation, corrosion, radiation, etc.). For aerospace applications, they should be as light as possible. Fiber-reinforced ceramic composites are most promising, and are attracting attention as materials that could meet these requirements.

With regard to ceramics having excellent heat resistance, new ceramics like high-strength silicon nitride and silicon carbide materials have recently been developed. But they suffer from the drawback of brittleness. They are very vulnerable to small cracks, and also weak to thermal and mechanical impacts.

Fiber-reinforced ceramic composite materials (CCMs) were developed to overcome this drawback. Thanks to their high strength at high temperatures, high toughness, and excellent impact resistance, CCMs are under active research mainly in Europe and the United States as promising structural materials with superhigh heat resistance. In particular, development and practical application research on CCMs have made the most progress by using the SiC fiber called Nicalon, which is marketed as a heat-resistant ceramic fiber and is widely used for practical purposes.

This report will deal with the characteristics of the Nicalon fiber and Nicalon fiber-reinforced ceramic composites.

## 2. Characteristics of Nicalon SiC Fiber

The Nicalon SiC fiber is a continuous long fiber whose main ingredient is  $\beta$ -SiC. It is made by spinning polycarbosilane, an organic silicon compound, making it infusible, and sintering it. The fiber has been commercialized by the Nippon Carbon Co., which started producing it in 1985 at a monthly rate of one ton for shipments both at home and abroad, including European countries and the United States. Table 1 shows Nicalon's general characteristics.

Table 1. General Characteristics of Nicalon

	Ceramic grade NL-200	HVR grade NL-400	LVR grade NL-500	Carbon coated NL-607
Diameter ( $\mu\text{m}$ )	14/12	14	14	14
No. of filaments (filament/yarn)	250/500	250/500	500	500
Tex (g/1000m)	105/210	110/220	210	210
Tensile strength (MPa)	3,000	2,800	3,000	3,000
Tensile modulus (GPa)	200	180	220	220
Elongation (%)	1.4	1.6	1.4	1.4
Density ( $\text{kg}/\text{m}^3$ )	2,550	2,300	2,500	2,550
Specific resistivity ( $\Omega\text{-cm}$ )	$10^3\text{-}10^4$	$10^6\text{-}10^7$	0.5-5.0	0.8
Coefficient of thermal expansion ( $10^{-6}\text{K}$ )	3.1	—	—	3.1
Specific heat ( $\text{J}/(\text{kg}\cdot\text{K})$ )	1,140	—	—	1,140
Thermal conductivity ( $\text{W}/(\text{m}\cdot\text{k})$ )	12	—	—	12
Dielectric constant (at 10 GHz)	9	6.5	20-30	—
Applications	Heat resistant materials, PMC, MMC, CMC	PMC	PMC	CMC

NL-200 and NL-607 are the CCM reinforcing fibers. NL-607, which is NL-200 coated with carbon by chemical vapor deposition (CVD), is an SiC fiber dedicated to CCM reinforcing. It features improved fiber-matrix interface matching, which is most important to CCMs. Nicalon is a continuous long fiber with a diameter of 15  $\mu\text{m}$ . The standard number of filaments is 500. Nicalon's characteristics are explained below.

(1) Lightweight, high strength, and high elasticity.

(2) Because of its excellent resistance to heat and oxidation, Nicalon maintains its high strength and high elasticity at high temperatures in the

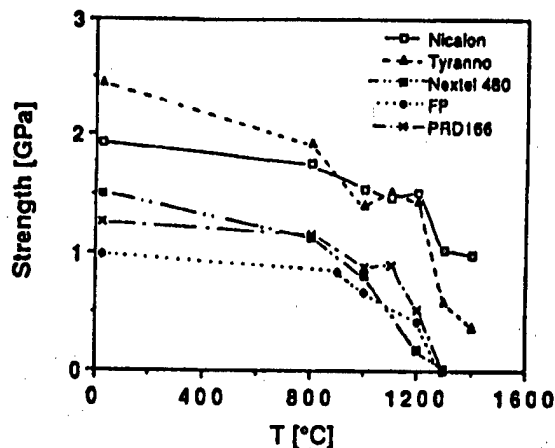


Figure 1. High-Temperature Strength of Various Ceramic Fibers

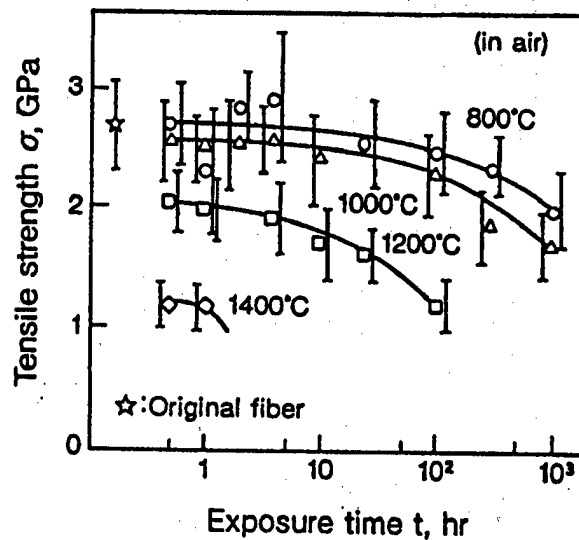


Figure 2. Strength Change of Nicalon After Exposure to High Temperatures

atmosphere. In a burner test, in particular, in which a weight is hung from the fiber and the fiber is heated by a gas burner, Nicalon shows better heat resistance than any other ceramic fiber. Figure 1 shows the changes in the strength of Nicalon at high temperatures in the atmosphere, compared to various ceramic fibers (Tyranno fiber and alumina fiber). It shows that Nicalon has the highest heat resistance among various fibers. Figure 2 shows the changes in tensile strength at room temperature after Nicalon is exposed to high-temperature air for a long time. Temperatures are 1,000°C for long-time exposure and 1,200°C for short-time exposure.

(3) Nicalon has good dimensional stability because of its small thermal expansion coefficient.

(4) As it is a thin, resilient continuous long fiber, Nicalon can be processed into various shapes like cloth, braids, and ropes.

(5) Nicalon matches well with resins, metals, and ceramics, and thus is effective as a reinforcing fiber for composites.

### 3. SiC Fiber-Reinforced Ceramic Composites

Nicalon is widely used as a reinforcer because it has the best matching characteristics as a reinforcing fiber for ceramic composites. Alumina fiber, which also is a ceramic fiber, cannot be used as a reinforcer because it reacts with the ceramic matrix.

Various composite forming methods are used for long fiber-reinforced ceramics, depending on the kinds of ceramics used as the matrix. here, I will classify Nicalon-reinforced ceramic composites by matrix and discuss forming methods and characteristics.

### 3.1 Glass/Glass Ceramic Composites

Prewo and others of the United Technology Research Center in the United States test-manufactured a Nicalon-reinforced glass composite in 1980, and demonstrated it has excellent strength and fracture toughness at high temperatures. This announcement triggered CCM research and development.

#### (a) Composite Forming

Matrix glasses include borosilicate glass (Pyrex), a heat-resistant glass made by Corning Glass Works of the United States, and lithium aluminosilicate (LAS, pyroceram used for heat-resistant tableware) which is crystallized glass.

Figure 3 shows a forming process for composites called the lay-up method. Nicalon yarn is continuously impregnated with a glass powder slurry. The fibers become impregnated with the glass powder, and are then taken up onto a rotating drum (mandrel) at a constant pitch to make a unidirectional tape. The tape is then cut into prescribed sizes, which are then stacked according to a preset number. Each stack is placed in a graphite die where it is hot pressed in an argon gas

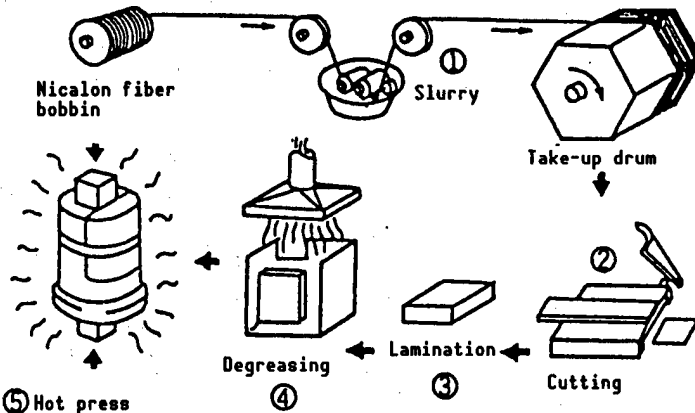


Figure 3. Composite Process of Fiber-Reinforced Glass Composite (Lay-up method)

atmosphere at a heat resistance of 1,300~1,500°C so that the fibers will become impregnated with molten glass to make a glass composite plate. The composite is heat processed again at a heat resistance to crystallize the glass in order to turn the matrix into ceramic with good heat stability.

#### (b) Characteristics of Composites

Figure 4 shows changes in high-temperature flexural strength of a Nicalon-reinforced LAS composite. Nicalon/glass composites not only have high strength at room temperature, but the strength increases at high temperatures. The increase occurs immediately before the temperatures where the matrix melts and softens. The flexural strength of a Nicalon/LAS (unidirectionally reinforced) is 900 MPa at 1,000°C.

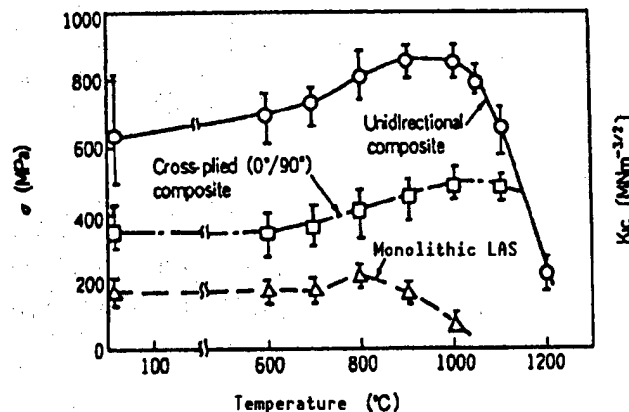


Figure 4. High-Temperature Flexural Strength of Nicalon/LAS Composite

No materials, even nickel- or cobalt-based heat-resistant steel, can

maintain such a high level of strength at such high temperatures, and the strength of the composite is better than that of recently developed fine ceramic silicon nitride. Another advantage is that its density is  $2.5 \text{ g/cm}^3$ , only one-third of heat-resistant steel.

Figure 5 shows the changes in fracture toughness ( $K_{IC}$ ) of glass composites. The fracture toughness of the Nicalon/LAS composite is  $17 \text{ MPa}\sqrt{\text{m}}$  at room temperature, and  $25 \text{ MPa}\sqrt{\text{m}}$  at  $1,000^\circ\text{C}$ . That of Norton's silicon nitride material (NC-132) is  $4.5 \text{ MPa}\sqrt{\text{m}}$  at room temperature, which means the Nicalon/LAS composite's toughness is more than three times greater than that of silicon nitride. As its fracture toughness is not much different from that of 2024-T<sub>6</sub> aluminum alloy, which is,  $22 \text{ MPa}\sqrt{\text{m}}$ , the Nicalon/LAS composite is practical enough for use as a structural material for machines.

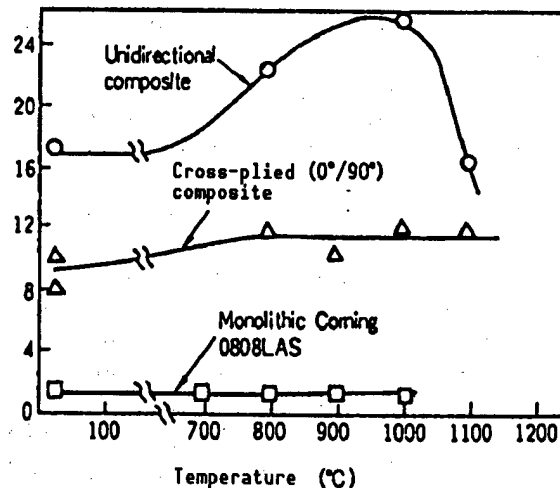


Figure 5. High-Temperature Fracture Toughness of Nicalon/LAS Composite

Its Charpy impact strength is also high, five times that of silicon nitride without a notch and more than 50 times with a notch. Silicon nitride is extremely vulnerable to a notch, whereas a composite of this type is little affected by it. Its thermal expansion coefficient is low at  $2.2 \times 10^{-6}/^\circ\text{C}$ , which provides good dimensional stability.

Thus, the Nicalon-reinforced glass composite is suitable as a lightweight heat-resistant structural material in that it is light, has high strength and toughness even at temperatures as high as  $1,000^\circ\text{C}$  in the air, and enjoys good dimensional stability. But because the matrix is glass, its heat resistance is limited compared with other ceramics. However, a calcium aluminosilicate (CAS) composite that can resist heat up to  $1,300^\circ\text{C}$  has recently been developed.

### 3.2 SiC Matrix Composite

#### (1) CERASEP

First, let me discuss an SiC fiber (Nicalon)-reinforced SiC composite developed and commercialized by SEP of France (trade name: CERASEP).

##### (a) Composite Forming Method

SiC is infiltrated into a preform made of laminated Nicalon fabrics or three-dimensional fabrics by the chemical vapor infiltration (CVI) method to create a composite. As shown in Figure 6, the preform is heated to a high temperature of  $1,000\text{--}1,200^\circ\text{C}$ , and methyltrichlorosilane ( $\text{CH}_3\text{SiCl}_3$ ) gas is introduced together with hydrogen gas. As silane gas dissociates into silicon and carbon at a high temperature, it deposits on the preform fiber surface as SiC.

Actually, various measures are taken during the process to ensure a uniform infiltration of the gas into the preform. Gas infiltration is usually done in a decompressed environment. Other processes that are used include Type 2, under which there are temperature differences on the preform; Type 3, under which there are pressure differences; Type 4, under which there are differences both in temperature and pressure; and Type 5, or the pulsed CVI method, under which gas is intermittently introduced. SEP has not disclosed the method it uses to produce CERASEP, but it is presumed to be Type 4. It is possible to make composites of various shapes by changing the preform shape. The CVI method can provide high-performance materials, but it takes a long time of two to several weeks to produce a composite, and it requires huge facilities, resulting in very high material costs.

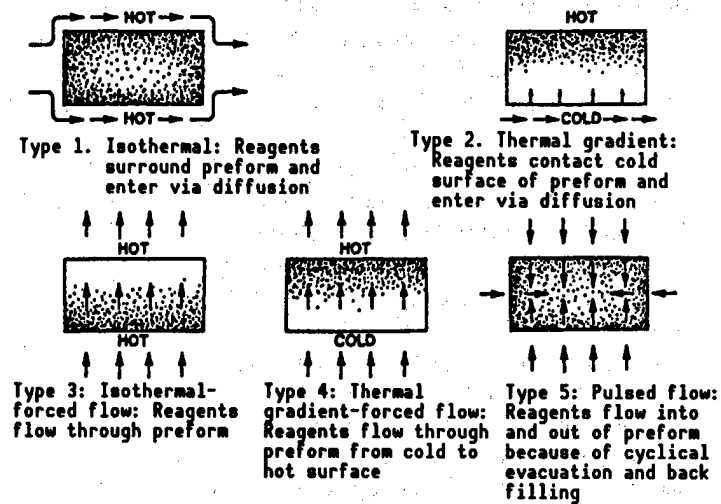


Figure 6. Various CVI Methods

Five general types of CVI processes. The long arrows represent flowing reagent; the short arrows show reagent diffusion. The progression of densification is indicated by shading; the heavier shading denotes more deposition.

## (b) Characteristics

Table 2 shows the characteristics of CERASEP reinforced in two directions (2D). Its specific weight is light at 2.5, and high strength and toughness are maintained at high temperatures, with flexural strength and fracture toughness standing at 280 MPa and 30  $\text{MPa}\sqrt{\text{m}}$ , respectively, at 1,400°C.

## (2) Nicaloceram

Next, I will explain a Nicalon/SiC composite (trade name: Nicaloceram) developed and commercialized by Nippon Carbon.

### (a) Composite Forming Method

Figure 7 shows the composite forming process of Nicaloceram. Prepregs are made by impregnating a Nicalon fabric with a slurry made of a denatured solution of polycarbosilane, the material of Nicalon fiber, and SiC powder. The prepregs are laminated into a certain shape and formed by hot press or autoclave molding. It is then hardened and sintered to make a Nicalon/SiC composite. Further, the composite is impregnated with polycarbosilane and sintered. This process is repeated several times to make the matrix denser. Finally, it is sintered at a temperature of 1,200°C or higher to obtain Nicaloceram.

Table 2. General Characteristics of Nicalon-Reinforced SiC Composite (CERASEP)

	23°C	1,000°C	1,400°C
Fiber content %	40		
Specific weight g·cm <sup>-3</sup>	2.6		
Pore rate %	8~15		
Tensile strength MPa	200	200	150
Elongation (tensile) %	0.3	0.4	0.5
Young's modulus (tensile) GPa	230	200	170
Poisson ratio vl-2	0.15		
Poisson ratio vl-3	0.40		
Flexural strength MPa	300	400	280
Compression strength // MPa	580	480	300
Compression strength ⊥ MPa	420	380	250
Shearing strength MPa	40	35	25
Thermal diffusion // 10 <sup>-6</sup> m <sup>2</sup> s <sup>-1</sup>	12	5	5
Thermal diffusion ⊥ 10 <sup>-6</sup> m <sup>2</sup> s <sup>-1</sup>	6	2	2
Expansion coefficient // 10 <sup>-6</sup> ·K <sup>-1</sup>	3		
Expansion coefficient ⊥ 10 <sup>-6</sup> ·K <sup>-1</sup>	2.5		
Fracture toughness MPa√m	30	30	30
Specific heat J·kg <sup>-1</sup> K <sup>-1</sup>	620	1,200	
Total radiation	0.75~0.80		

Thus, the forming method of Nicaloceram is similar to that of fiber-reinforced plastics (FRP), forming is easier for other ceramic composites, and it is possible to make large objects measuring 1 meter to thin objects only 0.5 mm thick. Plates, cylinders, and various other shapes can be made.

#### (b) Properties

Nicaloceram's properties are shown in Table 3. They are the properties of a Nicaloceram flat sheet made by laminating Nicalon plain cloth. Fiber volume content is 30 percent. Its density is not only lighter than metals, but also

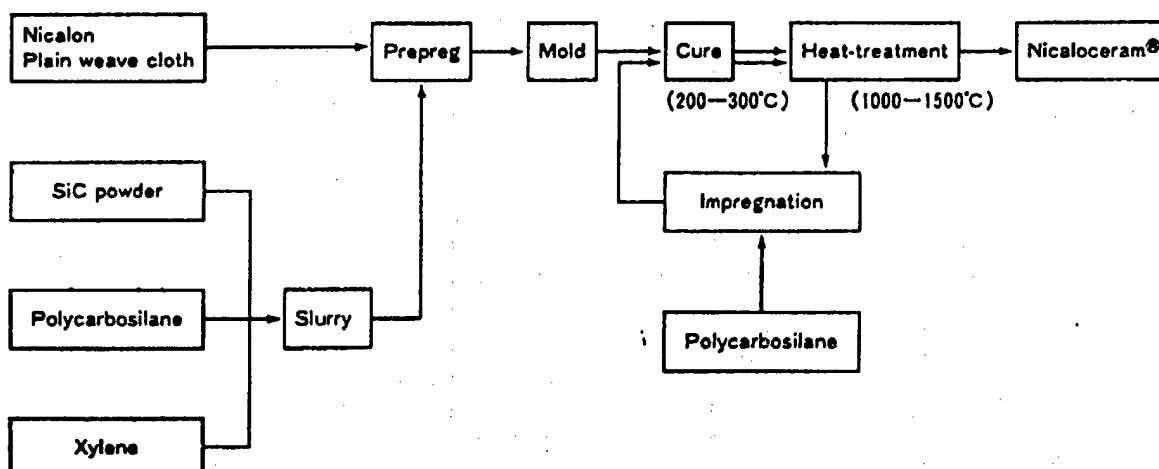
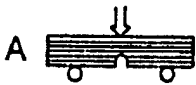
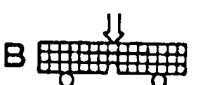


Figure 7. Nicaloceram Manufacturing Process

Table 3. Typical Properties of Nicalon/SiC Composite (NICALOCERAM™)  
(Plain cloth reinforcement)

Density (kg/m <sup>3</sup> )	1.9 x 10 <sup>3</sup>
Fiber volume (%)	30
Tensile strength (MPa)	110
Tensile modulus (GPa)	50
Flexural strength (MPa)	110
Flexural modulus (GPa)	40
Fracture toughness (K <sub>IC</sub> , MPa√m)	5 <sup>1)</sup> 9.5 <sup>2)</sup>
Coefficient of thermal expansion (K <sup>-1</sup> )	3.6 x 10 <sup>-6</sup>
Thermal conductivity (Wm <sup>-1</sup> K <sup>-1</sup> )	0.56 (at 773 K) 0.73 (at 973 K)
Specific heat (Jkg <sup>-1</sup> K <sup>-1</sup> )	1,130 (at 773 K) 1,170 (at 973 K)
1) Fracture toughness (K <sub>IC</sub> )      2) Fracture toughness (K <sub>IC</sub> )  	

general ceramics. Its flexural strength is similar to that of mullite, but its fracture toughness is higher than that of general ceramics at 6-9 MPa√m, because it is a fiber-reinforced composite. As the amount of fracture work also is large, Nicaloceram won't fracture all at once.



Figure 8 shows Nicaloceram's flexural strength after being exposed to a high-temperature atmosphere. It falls at 1,300°C, but does not change thereafter even after exposure for 100 hours. Figure 8 shows the results of a repeated thermal shock test under which the composite is immersed in water immediately after being heated to a high temperature. Its strength does not change even when the composite is subjected to thermal shocks produced by a temperature difference of 800°C. Ceramics generally are vulnerable to thermal shocks and crack when immersed in water after heating. The table shows that the fiber-reinforced composite is superior to them in terms of thermal shock resistance.

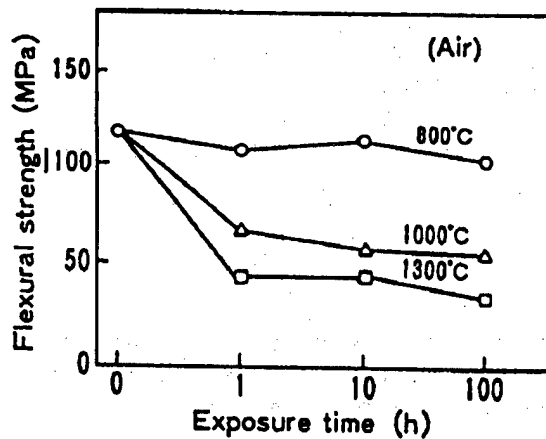


Figure 8. Flexural Strength of Nicaloceram After Exposure to High Temperatures

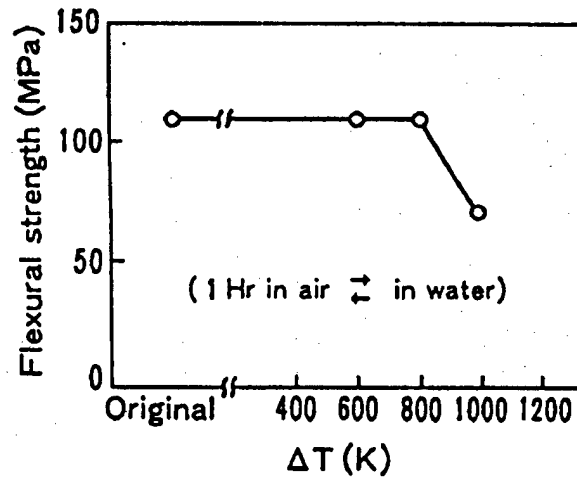


Figure 9. Thermal Shock Test of Nicaloceram

## **Development of Nano, Functionally Gradient Composites**

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[Article by Toshio Hirai, Tohoku University]

### **[Text] 1. Introduction**

Materials increasingly are being used in harsh environments, and the development of new composites with important properties is called for to create materials with superhigh resistance to severe environments.

A number of composites are attracting considerable attention as practical materials. These include fiber-reinforced composites, typical of which are fiber-reinforced plastics and carbon/carbon (C/C) composites. But totally new thinking that is not shackled by conventional concepts will be necessary to create the next generation of composites with superhigh environmental resistance.

I have been proposing nano composites that contain superfine dispersion phases, fine composites having elements as dispersion phases, and functionally gradient composites in which the distribution of dispersion phases is not uniform but changes continuously.

In this report, I will first take up nano and fine composites, which became the base of functionally gradient materials. Such materials were first proposed in Japan, and research on them is now being conducted worldwide. Next, I will explain the progress of development from nano composites by chemical vapor deposition (CVD) to gradient composites. Finally, I will discuss CVD synthesis, and the characteristics of SiC/C functionally gradient composites, which are now attracting attention especially for use as shields to protect against superhigh temperatures in space planes.

### **(2) In-Situ Composite Making**

Various manufacturing methods have been adopted for composites. These can be broadly classified into the phase bonding and phase separating (in-situ) methods.

In the case of ceramics, typical of the former method is the mixed sintering method. The latter method involves making a composite by turning heterogeneous materials into homogeneous ones (gaseous, fused, liquid, and solid). It is also called the in-situ composite formation method. A composite made by this method is sometimes called an in-situ composite.

### 3. In-Situ Composite Formation by CVD

Molded ceramics are usually made by sintering a material powder. Unlike oxide ceramics, sintering of nonoxide ceramics is difficult, and a sintering agent is often added to facilitate the process. Because this is a complicated process involving such tasks as powder adjustment, mixing, forming, preliminary sintering, and sintering, it is not easy to control the properties of the sintered ceramic composites.

CVD, on the other hand, adds energy to material gases to decompose the gases or cause a chemical reaction in order to obtain a solid. Therefore, it is possible to make a very high-density film or sheet without using a sintering agent. Further, in-situ composite formation can be achieved easily by introducing many kinds of material gases into a reactor simultaneously.

Figure 1 shows an example of a simple laboratory-scale CVD system.

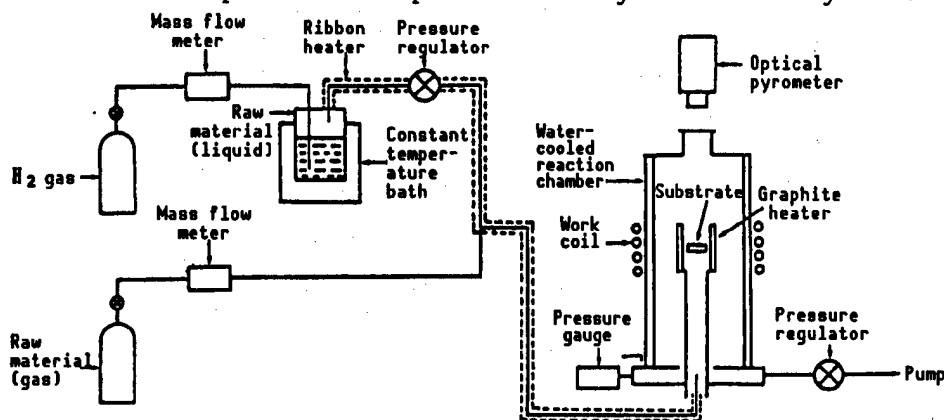


Figure 1. CVD Setup for Fabricating In-Situ Ceramic Composites

### 4. CVD Nano Composite

Professor Roy of Pennsylvania State University has synthesized a composite ceramic powder whose dispersion phase size ranges from several nanometers to dozens of nanometers, using the solution/sol-gel method. He broadly describes such materials as nano composites. But as the material was a powder, the details of the nano composite structure and its properties were unclear.

My group has succeeded in synthesizing sheet and film in-situ ceramic composites through the simultaneous decomposition of many material gases using CVD. At the same time, we have been able to clearly define their structures and properties. In composites of this type, the size of a dispersion phase is on the order of nanometers, and there are new characteristics that cannot be explained by the conventional rules for composites.

The structures of nano composites made by CVD vary as Figure 2 shows. These nano composite structures can be controlled by CVD conditions and the kinds of material gases used. Figure 2 also shows these examples.

### 5. CVD-Fine Composite

Conventional composite formation involves the mixing or combining of matrix substances and dispersion phase substances. But I recently proposed designing composites with "substance+element" combinations, a new idea that represents a departure from the conventional "substance+substance" idea, in order to develop new materials. It does not limit the dispersion phase to solids, and uses various elements as the dispersion phase, as shown in Table 1.

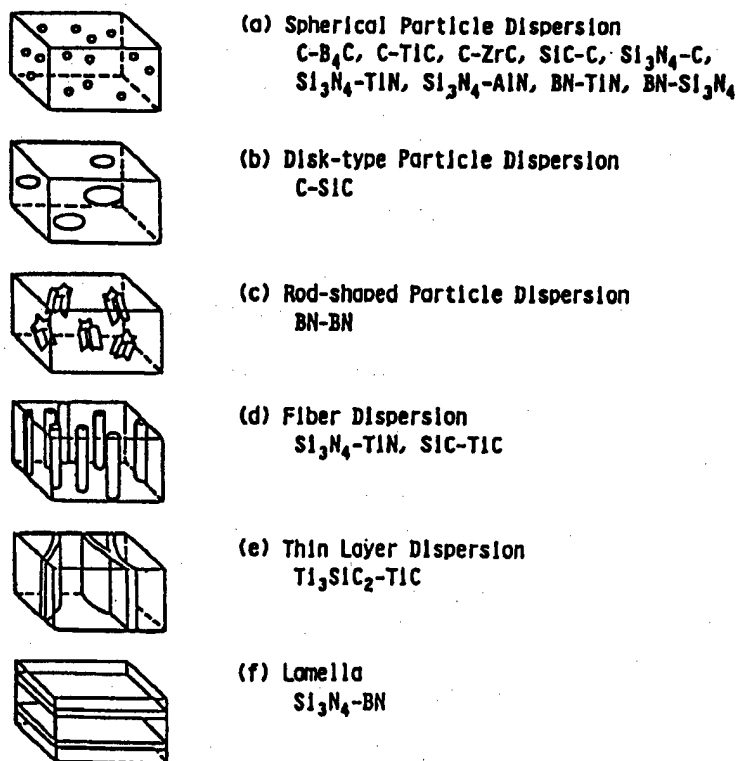


Figure 2. Nano-Structures of CVD Nano Composites  
Examples: In A-B, A is matrix and B is dispersion.

Table 1. Elements To Be Considered in Synthesis of CVD Fine Composites

Elements	Examples
Morphology of dispersion	Sphere, rod, fiber, flake, lamella
Type of dispersion	Solid, vapor (void, pore), liquid
Structural combination	Crystalline, turbostratic, amorphous
Boundary	Matching, reaction
Dispersing state	Uniformity, continuity

Composite synthesis based on this idea uses combinations of nonsubstances, for example, dispersion of lattice irregularities and defects, or very fine voids in the matrix, or the use of different crystal structures or orientation, even if the dispersion phase and the matrix have the same chemical composition and are the same substances.

A few examples are given below.

CVD SiC crystal grains have many lamination defects. These lamination defects change the direction of a crack, and increase fracture toughness. In this case, lamination defects can be regarded as dispersion phases.

In a CVD BN-BN composite, the matrix is BN with an irregular lamination structure, while the dispersion phase is crystalline (hexagonal) BN. Controlling the shape and dispersion amount of crystalline BN should make it possible to reduce lamination separation, a disadvantage of BN.

Before a superconducting oxide film can be put to use in the energy sector, it must have a high critical current density ( $J_c$ ) even in a high magnetic field. To this end, it is necessary to introduce some kind of "element" that is effective in pinning the vortex line.

In synthesizing YBCO-based superconducting oxide film using CVD, we used the crystal orientation (a-orientation) as the "element" together with superfine, Cu-rich disk-shaped deposition as the nano dispersion phase to make fine and nano composites. At 77 K and zero magnetic field, the superconducting film showed a  $J_c$  of about 2 million A/cm<sup>2</sup>, and about 60,000 A/cm<sup>2</sup> even at 27 tesla. The nano composite structures of the superconducting oxide film are shown in Figure 2 (b), (d) and (e). The dispersion phase is the Cu-rich superfine dispersion phase in (b), and CuO in (d), and a-orientation grains in (e).

#### 6. Composite Factors in Making Nano and Fine Structures

Nano and fine composites show interesting characteristics that cannot be predicted by the composite rules used to explain the characteristics of conventional micro composites. This is because the very small size of the dispersion phase, and the use of the dispersion phase as the element generate many composite factors, as shown in Figure 3. What influence these factors have on the characteristics of composites is an important topic for future research.

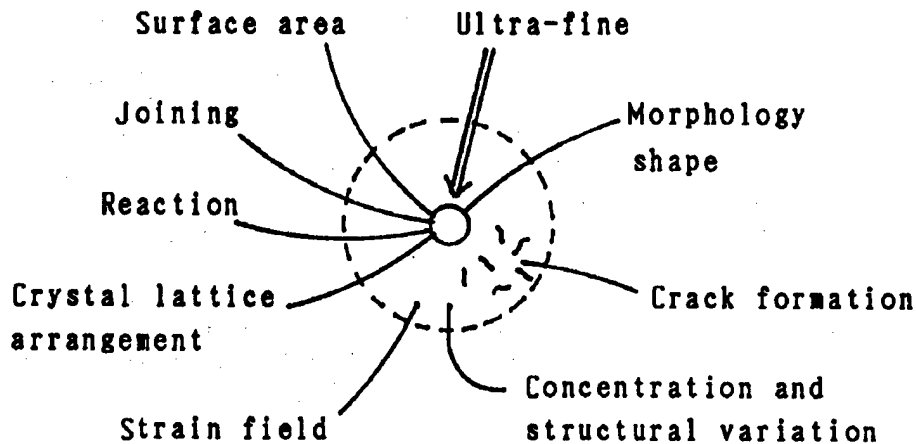


Figure 3. Parameters of Nano and Fine Composites

#### **(7) Development of New Materials Using Unevenness: FGM**

In ordinary composites, dispersion phases are dispersed uniformly in the matrix. However, we attempted to give composites new characteristics by unevenly (could be continuous in very small sections) dispersing dispersion phases (substances, elements).

In an  $\text{Si}_3\text{N}_4$ -C fine composite where amorphous C with a grain diameter of hundreds of nanometers is dispersed in amorphous CVD  $\text{Si}_3\text{N}_4$ , the C grains form a three-dimensional network, and the addition of only 0.2 wt% of C boosts conduction by 10 digits [as published].

Functionally gradient materials (FGMs) are now attracting attention worldwide as new materials in which locally different functions can be added to a single material by continuously changing dispersion phase density, kinds or structure from one side of the material to the other, or by changing them locally to alter its characteristics.

The development of materials that are resistant to superhigh temperatures will be needed for the development of completely reusable space shuttles. In this case, one surface of the material would be exposed to a high-temperature (2,000 K) oxidizing atmosphere, while the other is cooled to 1,000 K. Thus, there is a temperature difference of 1,000 degrees in the material. Currently available materials cannot be used in such an extreme environment. Different materials stuck together will break because of the thermal stress generated within them.

Beginning in the summer of 1984, five researchers (including myself) gathered at my laboratory at the National Space Laboratory, Tohoku Government Industrial Research Institute, and Tohoku University, where we held a series of heated discussions. As a result, we found that a gradient material design is an effective way to ease thermal stress, and the proposed idea of "functionally gradient materials," which was based on a new concept.

FRM were taken up under a big project of the Science and Technology Agency that started in 1987. A research group made up mainly of heavy industrial companies was later set up, and active research was conducted. The first international conference on FGM was held in Sendai, Miyagi Prefecture, in October 1990, and it attracted researchers from around the world. The second international conference will take place in San Francisco in November 1992.

The term "functionally gradient materials" is now adopted by many academic societies and subcommittees, and working groups have been set up for the promotion of FGM research. The term also is being included in dictionaries, and has come to be recognized by the general public.

#### **8. Designing CVD SiC/C Functionally Gradient Composite**

In developing thermal stress-eased superhigh-temperature shields, various materials were studied. What was selected was a combination of silicon carbide (SiC), which has good resistance to oxidation at high temperatures and high

strength at high temperatures, and graphite (C) which matches well with a C-C composite, a structural material, and has a low Young's modulus and high thermal conduction. An SiC/C FGM has SiC on one side and C on the other, while its composition changes continuously from the SiC side to the C side.

In order to forecast an optimum gradient composition distribution for minimum thermal stress in an SiC/C FGM, imagine an infinite cylinder 10 mm thick and 95 mm in inner radius, one end of which is constrained (Figure 4). When the inside temperature is 1,600 K and the outside is 300 K with a 1,300 K temperature gradient thus generated, the stress status with zero stress in the axis direction can be calculated. It is assumed that the cylinder has an SiC single phase to a depth of 1 mm from the inner surface, a gradient composition (various properties) from SiC to C from 1 mm to 10 mm in the thickness direction, and an SiC/C functionally gradient film with a uniform composition distribution in the inside direction.

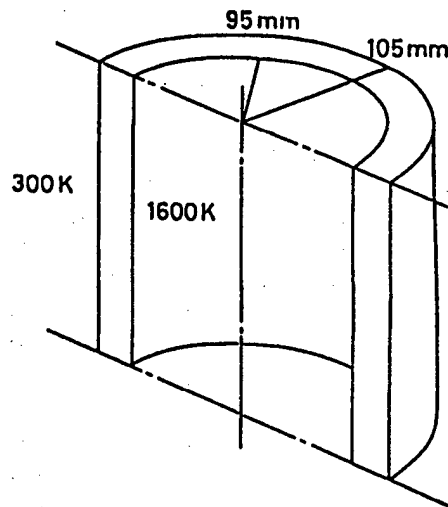


Figure 4. Cylinder Model for Calculation of Thermal Stress in SiC/C Functionally Gradient Composite (Inside: SiC; Outside: C)

The internal stress was obtained for various gradient compositions, and at various temperature gradient conditions. Figure 5 shows the stress distribution, temperature distribution, and Young's modulus distribution when the strength-internal stress ratio becomes 1 or lower, while Figure 6 shows the gradient composition at that time. It is clear from Figure 5 that in an SiC/C functionally gradient film, the composition gradient can slash the thermal stress to one-sixth that of the SiC single phase.

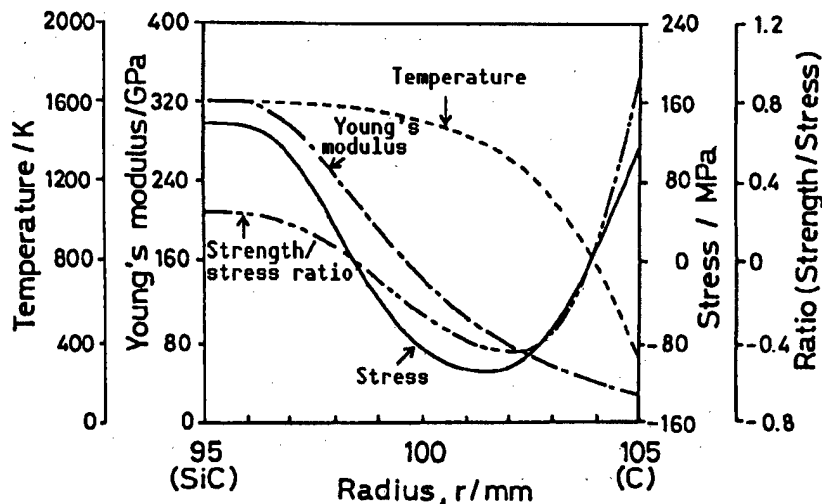


Figure 5. Calculated Distributions of Temperature, Young's Modulus, Stress, and Strength/Stress Ratio in SiC/C Functionally Gradient Composite

An SiC/C FGM having a gradient composition shown in Figure 6 was synthesized as CVD as follows.

The material gas was an  $\text{SiCl}_4 + \text{C}_3\text{H}_8 + \text{H}_2$  system, and the synthesizing temperature was 1,773 K. While keeping the flow of  $\text{C}_3\text{H}_8$  constant, the flow of  $\text{H}_2$ , the carrier gas for  $\text{SiCl}_4$ , was controlled to change the ratio of the material gas in steps under the conditions shown in Table 2. This method makes it possible to synthesize an SiC/C functionally gradient film whose composition changes continuously from SiC to C on a graphite substrate. The thickness of the film obtained by synthesis for 100 minutes was about 1 mm.

Figure 7 is a scanning electron microscope photo of a cross section of the SiC/C functionally gradient film. A dense SiC phase 150  $\mu\text{m}$  thick is generated on a graphite substrate, and there is an SiC/C functionally gradient film 800  $\mu\text{m}$  thick with voids in it. The ratio of SiC to C changes continuously, and a 50  $\mu\text{m}$ -thick C phase is made on it. A section with 10~90 mol% of dispersion phases has an especially large number of pores. Micropores exist because a change in the mixing ratio of gas containing Si and gas containing C affects the decomposition process in the vapor phase, resulting in a change in the crystal growth process of both SiC and C. Pores begin to appear when SiC begins crystal growth in a direction vertical to the deposition surface. The existence of pores serves to ease thermal stress.

In a region where a tiny amount of SiC is dispersed in the C matrix, the SiC size is dozens of Å, and the SiC has a flat sheet shape as shown in Figure 2(b). The amount of C changes the direction of SiC crystal growth. This demonstrates that the SiC/C functionally gradient film is both a nano composite and a fine composite as well.

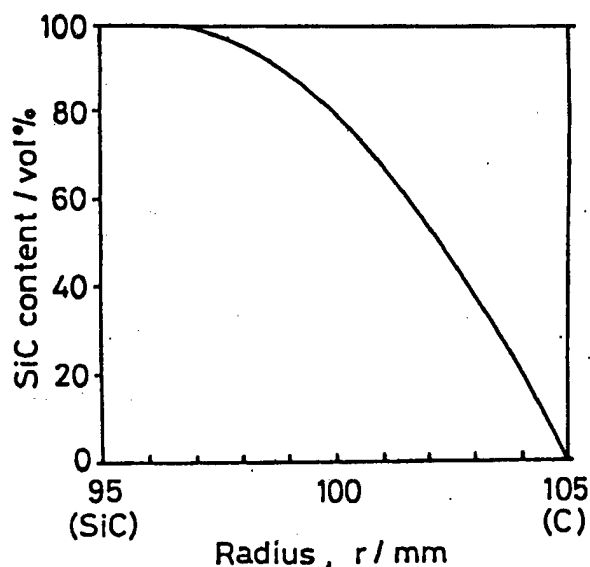


Figure 6. Suitable Compositional Distribution in SiC/C Functionally Gradient Composite Predicted by Calculation

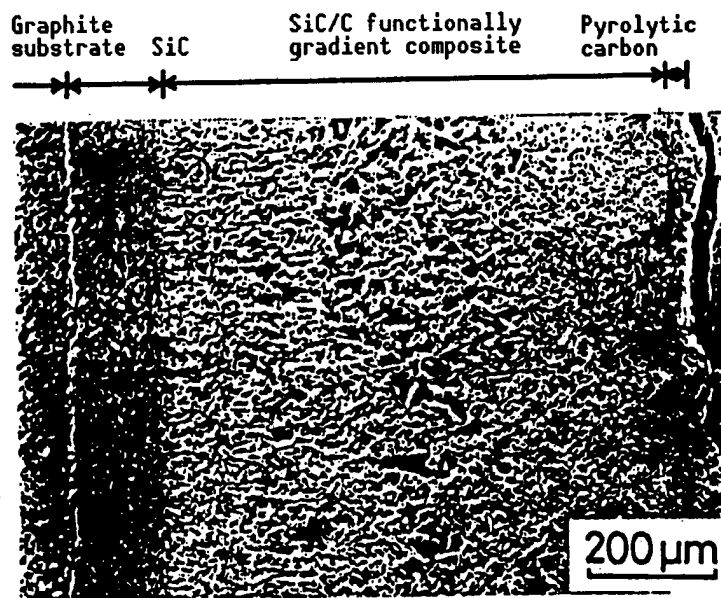


Figure 7. SEM Photograph of Cross-Sectional Surface of SiC/C Functionally Gradient Composite



Table 2. CVD Condition for Preparation of SiC/C Functionally Gradient Composite Using an  $\text{SiCl}_4 + \text{C}_3\text{H}_8 + \text{H}_2$  System

Deposition temperature, K	1,773					
Total gas pressure, kPa	6.7					
Si/(Si+C) in input gas	0.66	0.62	0.58	0.52	0.23	0
Deposition time, min	10	15	15	10	20	30

### 9. Characteristics of CVD SiC/C functionally gradient composite

We studied the thermal shock resistance of the SiC/C functionally gradient film. Figure 8 shows the results of the study. We compared it with a CVD SiC single phase, using a 5 kW  $\text{CO}_2$  laser thermal shock testing system (Mitsubishi ML50C). Figure 8 shows the relationship between laser power density and a calculated temperature difference in the film.

Laser power density necessary for generating a crack ( $\Delta$ ,  $\bullet$ ,  $\nabla$ ) was 5.8  $\text{MW}/\text{m}^2$ , but it was high at 7.4  $\text{MW}/\text{m}^2$  for the SiC/C functionally gradient film. When the thickness of the SiC/C functionally gradient film increased from 0.8 mm to 1.8 mm, the temperature difference inside the film rose from 390 K to 560 K. The SiC/C functionally gradient film thus has good resistance to thermal shock and is promising as a thermal stress-eased high-temperature shield material.

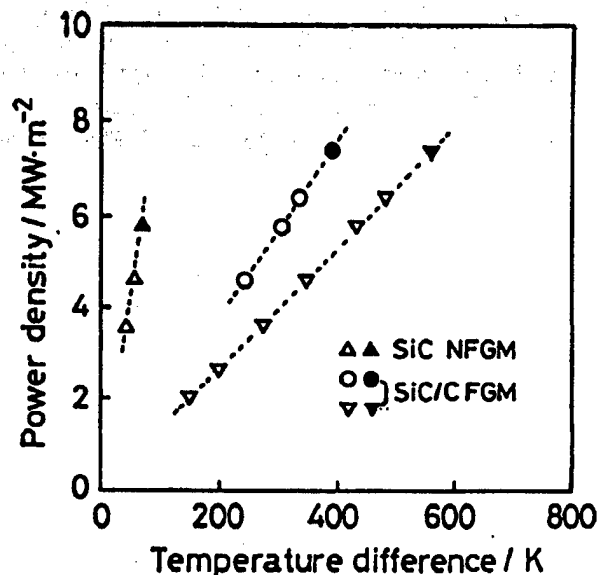


Figure 8. Relationship Between Laser Power Density and Calculated Temperature Difference in Thermal Shock Resistance Test  
(○: No cracking; ●: Cracking)

### 10. Conclusion

This report has demonstrated that superfine control of composite structures, or nano composites, and the combining of elements, or fine composites, can produce new materials.

Current industrial materials were developed as the result of a homogenization process, and any section of single material has the same characteristics as the rest. However, all the things that exist around us in nature are heterogeneous materials.

The fiber structure continuously changes in bamboos and trees. Likewise, the laminated structure in shells, and the inorganic-organic composite structure in bones also changes. These are functionally gradient materials. The move to develop new materials by unevenly dispersing (gradient) dispersion phases, as in nano composites and fine composites, is an attempt to learn from the wisdom of nature.

This report took up the CVD SiC/D functionally gradient film as an FGM, and introduced part of it.

As explained earlier, FGM research started in order to develop structural materials with eased thermal stress, emphasizing mechanical functions at high temperatures, with the development of spaceship materials in mind. But the proposers of FGM, including myself, have believed from the beginning that the advantages of FGM can really be used in the fields of energy, electronics, optics, and biology. The application of FGM in these fields has been adopted for the Science and Technology Agency's project for the new fiscal year, and the further development of FGM is widely expected.

- END -